Nanometric material removal using electrokinetic phenomenon

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**NANOMETRIC MATERIAL REMOVAL USING
ELECTROKINETIC PHENOMENON**

LEO CHENG SENG

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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A thesis submitted to the Nanyang Technological University
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Doctor of Philosophy

2012

To my wife and daughter...

Abstract

Material removal at the sub-micron level has been a topic of interest in the past few years, particularly with respect to the fabrication of miniaturized devices. While numerous techniques have been developed and refined from their larger meso-scale counterparts (e.g. polishing), most have inherent limitations (such as the introduction of scratches from polishing) which may render these processes to be less attractive.

In this work, a novel non-contact technique (where the machining tool is not in contact with the workpiece [1-4]) of using electrokinetic phenomenon for precise material removal (a.k.a electrokinetic material removal process) at rates in the order of nanometers/min is introduced. The technique involves movements of abrasive particles in a fluidic flow, under the influence of an AC electric field with a DC offset, to collide with the surface of the material to achieve material removal.

Results showed that the technique is feasible in achieving material removal up to a depth of several hundred nanometers. Parametric studies on the material removal, which include material removal rate (MRR) and surface roughness (SR), were carried out and documented. A semi-empirical model on the material removal rate (MRR) was subsequently proposed after the dominating material removal mechanism was identified. The model was further validated with additional experimental results to show its predictive capability.

With no chemicals involved in the process, the technique offers the further attraction of being a benign nano-manufacturing process with potential usage in the microelectromechanical systems (MEMS) areas.

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Nomenclature

a = acceleration of the object (m/s^2)

a_y = acceleration of the particle in the Y direction (m/s^2)

A = cross sectional area of the channel (m^2)

A_s = surface area between polishing pad and workpiece (m^2)

C_D = frictional coefficient

C = constant that is related to the amount of the particles impacting onto the surface of the workpiece

$Conc_{original}$ = concentration of the particles in the slurry upon preparation before the material removal process

$\left(\frac{dy}{dt}\right)$ = particle's speed (m/s)

D_H = hydraulic diameter of the channel (m)

e = fundamental electric charge

E = applied electrical field (V)

E_{DC} = DC electric field (V/m)

E_{AC} = AC electric field (V/m)

f = frequency of the AC voltage applied (Hz)

f_{CM} = Clausius Mossitti factor

$f(conc)$ = function relating to the effect of the concentration of the abrasive particles on the material removal rate of the process

F_B = buoyancy force (N)

F_G = gravitational force (N)

F_{DEP} = dielectrophoresis force (N)

F_{Drag} = drag force (Nm)

F_{Drag_x} : drag force acting against the motion of the particle in the X direction (Nm)

F_{Drag_y} : drag force acting against the motion of the particle in the Y direction (Nm)

$F_{E(DC+AC)}$ = electrokinetic force (N)

F_{pump} = pumping force of the fluid acting on the particle (Nm)

F_X = forces in the X direction (N)

F_Y = forces in the Y direction (N)

g = gravitational acceleration (m/s^2)

h = instantaneous thickness of the gap between the planar wall surface and the closest point on the particle (nm)

H = height of channel (μm)

I_p = moment of inertia of the particle about its centre of gravity (kgm^2)

k_b = Boltzmann constant

k_1 = arbitrary constant

K_p = Preston coefficient

$K.E$ = kinetic energy of the abrasive particle (eV)

K = ratio of the vertical to the horizontal force components acting on the impacting particle

L = length of the channel (μm)

L_d = applied load (N)

m_p = mass of particle (kg)

M_{speed} = machining rate ratio

n_∞ = ionic number concentration in the bulk solution

$N_{during\ process}$ = number of layers of stacked abrasive particles throughout the channel under the electrokinetic effect during the material removal process

$N_{particles\ in\ each\ cycle}$ = number of particles in each cycle introduced into the channel

N_{cycle} = number of cycles each particle undergoes from the entry to the exit of the channel

p = flow pressure between the abrasive and the surface of the workpiece (related to hardness) (Pa)

p_f = pressure of the flow (Pa)

P_r = applied pressure (Pa)

P = constant that is related to the coefficient of friction between the abrasive particles and the surface of the workpiece

Q = volumetric flow rate (m^3/cm)

Q_E = surface charge of the colloidal particle (C)

r = radius of the particle (μm)

Re = Reynolds number

$\text{Re}[f_{CM}]$ = real part of f_{CM}

t = time (s)

$t_{\text{dwelling time of the abrasive particles on workpiece}}$ = dwelling time of the abrasive particles on the surface of the workpiece (s)

t_p = time taken for the abrasive particle to reach onto the surface of the workpiece during each cyclic collision (s)

t_{process} = time taken for the material removal process (s)

T_o = temperature (K)

T = period of each oscillation (s)

u = localized velocity of the fluid at the different position of the channel (m/s)

U = general velocity of the fluid flow (m/s)

V = volume of particle (m^3)

V_a = average relative velocity (m/s)

V_c = critical settling velocity of a particle just removed or deposited before flowing out (m/s)

V_p = net velocity of the abrasive particle (m/s)

V_s = settling velocity of the particle and V_c is the critical settling velocity of a particle just removed or deposited before flowing out (m/s)

V_x = velocity of the particle in the X direction (along the channel) (m/s)

V_y = velocity of the particle in the Y direction (perpendicular to the channel) (m/s)

V_0 = volume of the material removal (m^3)

V_{AC} = amplitude of the AC voltage applied (V)

V_{DC} = DC voltage applied (V)

$Vol_{channel \text{ in each cycle}}$ = supposed volume of the channel travelled by the trapped abrasive particles during each cycle (m^3)

w = width of the channel (μm)

$\dot{x}_t$ = velocity of the contacting tip of the particle (m/s)

y' = distance of the localized element of the fluid from the centre of the separation between the two electrodes (μm)

z = valency of the ions

α_p = angle of impingement ($^\circ$)

$\hat{\alpha}_p$ = angle of impingement for maximum material removal ($^\circ$)

$\alpha(h)$ = wall correction factor for drag force

γ = surface energy of the workpiece that has to be overcome for material removal to occur (eV)

ε = dielectric constant

ε_r = relative dielectric constant

ε_0 = permittivity of vacuum

ε^* = complex electrical permittivity

ε_p^* = complex electrical permittivity of the particle

ε_m^* = complex electrical permittivity of the medium

η = fluid viscosity (mPas)

$\eta_{\text{efficiency_trapping}}$ = trapping efficiency of the particles during each cyclic collision with the surface of the workpiece

$\eta_{\text{efficiency_trapping_reservoir}}$ = trapping efficiency of the settling particles in a reservoir

κ^{-1} = Debye length (μm)

μ_{EOF} = electroosmotic mobility ($\text{m}^2/(\text{V}\cdot\text{s})$)

v_{EOF} = electroosmotic velocity (m/s)

ρ_f = density of the fluid (kg/m^3)

ρ_p = density of particle (kg/m^3)

ζ = zeta potential (mV)

σ = electrical conductivity (S/m)

$\sigma(h)$ = correction factor attached to the electrokinetic force expression for a sphere undergoing electrophoresis; it is associated with the differences in flow patterns between sedimenting vs electrophoretically driven spheres

τ_{speed} = shear stress ratio τ_{speed}

ω = frequency of the AC field signal in dielectrophoresis (Hz)

$\nabla \left| \vec{E} \right|^2$ = gradient of the square of the electric field quantifying the non-uniformity of the electric field

pk-pk = peak-to-peak

MRR = material removal rate ($\text{\AA}/\text{Hr}$)

SR = surface roughness (nm RMS)

μm = micrometer = 10^{-6} m

nm = nanometer = 10^{-9} m

$\text{\AA}$ = Angstrom = 10^{-10} m

List of publications

1. Leo CS, Blackburn TL, Ng SH, Yang C, Butler DL, Danyluk S. Nanometric material removal using the electrokinetic phenomenon. In: *Proceedings of SPIE - The International Society for Optical Engineering 6415*. (Canberra, ACT, Australia, 2007).
2. Leo CS, Blackburn TL, Ng SH, Yang C, Butler DL, Danyluk S. Precision material removal using the electrokinetic phenomenon. In *Proceeding of ASPE- American Society For Precision Engineering*. (Portland, Oregon, USA, 2008).
3. Butler DL. Alternative material removal approaches for planarization. In *Proceeding of ICPT- International Conference on Planarization/CMP Technology*. (Hsinchu, Taiwan, 2008).
4. Danyluk S, Blackburn TL, Butler DL, Leo CS. Environmentally benign material removal devices for the fabrication of microdevices. *Materials Science Forum*. 2009. Vols 620-622, pp. 451-456.
5. Leo CS, Butler DL, Ng SH, Yang C, Danyluk S. An alternative approach to planarization using the electrokinetic phenomenon. In *Proceeding of MRS- Material Research Society*. (San Francisco, California, USA, 2009).
6. Leo CS, Teo WG, Butler DL, Ng SH, Yang C, Danyluk S. Surface roughness study on material removal using electrokinetic phenomenon. In *Proceeding of ICMAT- International Conference on Materials for Advance Technologies*. (Singapore, 2009).
7. Leo CS, Ng SH, Yang C, Butler DL, Danyluk S. Influence of particle effects on the material removal rate utilizing electrokinetic phenomenon. *Advanced Materials Research*. 2009. Vols 76-78. pp 27-32.
8. Leo CS, Chua JCM, Ng SH, Yang C, Danyluk S, Butler DL. An investigation in material removal using electrokinetic effects on abrasive particles. In *Proceeding of ICAM- International Conference on Materials Advanced Manufacture*. (Kenting, Taiwan, 2010).

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10. Leo CS, Butler DL, Ng SH, Danyluk S. Influence of electrochemical dissolution effect on the material removal rate utilizing electrokinetic phenomenon. *Advanced Materials Research*. Vols. 126-128 (2010) pp 873-878.
11. Leo CS, Butler DL, Ng SH, Danyluk S. Electrokinetic abrasive machining - an alternative approach to material removal. In *Proceedings of Nanoman - International Conference on nanoManufacturing*. (Tianjin, China, 2010).
12. Leo CS, Butler DL, Ng SH, Danyluk S. An investigation on the influence of particles on the material removal rate utilizing electrokinetic phenomenon. In *Proceedings of CIRP - International Conference on High Performance Cutting*. (Gifu, Japan, 2010).

Chapter 1

Introduction

This chapter presents a brief introduction into the research work. The introduction covers the background, motivation, objectives and scope of the project. Subsequently, an outline of the report is included (Fig 1.1) to reveal the topics of the report that are about to be presented in the following chapters.

Fig 1.1 Overview of Chapter 1

1.1 Background

With advances in technology, a trend in product design and manufacturing of miniaturized devices has emerged [5]. These miniaturized products as well as the fabrication technologies are classified as microsystem technology (MST). MST has been identified as having an important role in manufacturing owing to its potential in producing miniature, light and functional devices [6,7]. In the near future, this trend will shift towards nanotechnology with the demand of producing even smaller devices with more functionality and better performance [7]. The curve presented by Taniguchi [8] and

updated recently by McKeown [9,10] in Fig 1.2 traces the development in manufacturing capabilities in terms of machining accuracy since the 1940s.

Source: McKeown [10] after Taniguchi [8]

Fig 1.2 Development of achievable machining accuracy since 1940s [10]

Today, MST has emerged as a possible technology for applications such as information technology (IT) peripherals, automotive, consumer electronics, life science and industrial process control [11]. According to a recent report coordinated by Semiconductor Equipment and Materials International (SEMI®) and Yole Développement, it is projected that MST will develop into a worldwide market exceeding US\$15 billion in the near future [12] as shown in Fig 1.3.

To realize the targeted growth of MST, one of the main criteria would be to improve the fabrication technologies that produce these miniature products. This can be fulfilled by either optimizing the existing fabrication machineries or by developing novel fabrication techniques that enable better precision and machining features for future manufacturing needs.

Fig 1.3 Total market for microelectromechanical systems (MEMS) and MST products [12]

Due to the rapid progress in the miniaturization technology, there is a shift in the demand in dimensional accuracy of devices from the order of micrometers (10^{-6} m) to nanometers (10^{-9} m). Hence, the interest in fabricating miniaturized devices has led to the need to develop techniques capable of removing material precisely and at a relatively low removal rate [1].

Currently, the available technologies that are widely used for the micromachining of miniature devices include microcutting technologies (e.g. microgrinding [13-16] and micromilling [14,15,17,18]), electrothermal processes (e.g. micro electrical discharge machining (μ EDM) [19] and laser machining [14,20,21]), chemical processes [22,23] and free abrasive machining [8,24,25]. However, each of these micromachining methods has their limitations in their respective processes. Microcutting systems are traditional machining processes that involve the mechanical interaction of a sharp tool with the workpiece to cause breakage in a defined path and achieve material removal in the form of chips. Due to this interaction, one of the major implications of the process is the high

machining force acted by the working tool that causes the deflection and even breakage of the tool with the workpiece [26]. Another critical issue of the microcutting technique is the high precision of the tool holder that can accurately position the tool during the machining process [14] where, presently, microcutting in the region of 5 nm positional accuracy has been reported [17]. To address these limitations, non-traditional machining methods such as electrothermal processes have been introduced. Electrothermal machining removes workpiece material by utilizing the melting and vaporizing mechanisms. In the process, the thermal energy that is provided with a heat source melts and vaporizes the material away. The more popular electrothermal techniques that are utilized are the μ EDM [27] and laser beam machining (LBM) processes [21]. These techniques hold the advantages of being able to machine all existing materials due to their machining characteristics as well as being non-contact processes. Owing to the fact of being non-contact processes, the techniques are not restricted by the machining forces that are acted upon the workpieces by the working tools. However, these techniques affect the surface quality of the workpiece during machining due to their thermal material removal mechanism. Some of the defects that result from these processes include microcracking, formation of heat affected zones (HAZ) and striations. Thus, in order to produce a very smooth surface with minimal affected layers or strain, which are the basic requirements for functional materials, chemical processes and free abrasive machining techniques are employed. Typically, chemical processes are dominated by the chemical reactions that remove the material from the surface. This causes the etching process to follow according to the initial contour of the workpiece before etching and does not perform any planarization action. In addition, chemical processes can be costly due to the disposal of the toxic by-products. An avenue to address these issues is through the introduction of free abrasive machining techniques. One of the common examples of free abrasive machining that provides planarization of the workpiece would be the polishing process. Polishing is carried out without letting fine abrasive particles generate brittle fractures on the work surfaces, while removing these materials in minute steps by means of micro elastic and plastic conditions, to finally produce a smooth mirror surface with minimal damages [1]. Conventional polishing technique involves the use of fine abrasive particles in a liquid carrier on a polishing pad. During the process, contact of the

workpiece, abrasives and polishing pad are observed. Since most of the polishing techniques involve interactions between the polishing pad and the workpiece, non-contact polishing approaches (where the machining tool is not in contact with the workpiece [1-4]) have attracted interest over recent years. This is because non-contact techniques minimize defects such as scratches that are typically caused by the polishing tool and workpiece interaction. Float polishing [2] and elastic emission machining (EEM) [3] are two of the processes that fall within this category. However, both processes are usually either not versatile or unable to achieve high machining throughput. Due to these limitations, alternative non-contact micromachining techniques are being sought and developed to add as alternative processes to the current ones.

1.2 Motivation

From Fig 1.2, free abrasive machining appears to be one of the candidates with the greatest potential in achieving nanometric material removal capability. In addition, free abrasive machining is relatively cheap as compared to the other material removal processes such as ion beam machining and molecular manipulation (where the latter processes require much higher precision movements as compared to the former one). Due to the cheaper means of achieving nanometric material removal, this makes free abrasive machining affordable and more readily acceptable for implementation. Free abrasive machining involves the use of abrasive particles within a medium to remove the workpiece material. Usually, the abrasive particles are agitated by a mechanical motion that embodies them with a considerable amount of impact velocity to collide with the workpiece for material removal. The process is undertaken by employing fine abrasives to remove the material on the surface of the workpiece in a minute material removal mechanism by means of micro elastic and plastic conditions without generating brittle fractures on it [1].

Over the past decade, particle trajectory manipulation under the influence of electric field has been an area of interest [28]. Research has been undertaken in manipulating the trajectories of the particles in various aqueous fluid [29,30]. Some of the applications

involve the separation and aggregation of particles [31]. The techniques that are used in the manipulation of the particles under the influence of electric field can be categorized as DC and AC electrokinetic effects [21]. These techniques will be discussed in more detail in the following chapter. Due to the capability of manipulating particles in fluid by using electrokinetic phenomenon, it is possible to project the abrasive particles in the slurries with a certain impact velocity to collide with the workpiece to cause nanometric material removal. Furthermore, this technique provides the added advantage of achieving material removal without the use of a cutting tool or a polishing load pad which implies that there is no pressure acting on the workpiece during machining. This results in achieving material removal with minimal damages or strain which is a basic requirement for miniature functional components.

1.3 Objectives of research

The research was carried out with the following aims:

- To introduce and demonstrate a novel non-contact material removal method (where the machining tool is not in contact with the workpiece [1-4]) that utilizes the electrokinetic phenomenon to achieve nanometric material removal
- To study the influences of the electrokinetic and hydrodynamic effects on the material removal rate
- To understand the material removal mechanism of the proposed process such that a semi-empirical model can be proposed to relate the material removal rate to the parametric conditions
- To study the influences of the electrokinetic and hydrodynamic effects on the surface roughness of the workpiece after the material removal process

1.4 Scope of research

The research is undertaken to look at the feasibility of using electric field activated abrasive particles to achieve material removal on a workpiece. Experiments will be carried out to study the fundamental aspects of the motion of the particles and the

material removal rates of the material removal process under the influences of various possible parameters in the experimental setup. A test structure consisting of a channel, between the base substrate and the workpiece where fluid can pass through, will be designed. Subsequently, an electrical voltage will be applied between the electrode and the workpiece to manipulate the abrasive particles which will generate material removal on the workpiece. Profile measurements will be conducted to measure the amount of material removed and determine material removal rate of the workpiece. The mechanism involved in the material removal will be determined before a semi-empirical model will be constructed to explain the relationships between the influencing parameters and the experimental results for the material removal rate (MRR). Experiments of the electrokinetic process would be carried out on another industrial material (aluminium) to demonstrate the feasibility of the process on the material and to further validate the material removal model for predictive capability. Consequently, the surface roughness of the workpiece under the influences of the electrokinetic and hydrodynamic effects will be documented together with the material removal rate (MRR) to determine their relationship such that the process can be controlled and optimized to precisely remove material while generating a finished surface with predetermined roughness.

1.5 Outline of thesis

The report will consist of eight chapters. The present chapter introduced the SEMI[®]/Yole Développement roadmap and covered an overview of the present micromachining processes with reference to the College International pour la Recherche en Productique (CIRP) keynote papers. In chapter 2, a critical review of the existing micromachining technologies will be presented to understand the need of a novel micromachining technique. At the same time, the fundamentals of electrokinetic effects will be reviewed to understand how it can be used to manipulate the motion of the particles in a fluidic medium. Several material removal mechanisms (such as mechanical and non-mechanical mechanisms) will also be reviewed in chapter 2 to give an insight into the material removal mechanism of the proposed process. Chapter 3 will cover the experimental methodology and the characterization techniques that are carried out to study the

machined features. Subsequently, in chapter 4, the chosen electrokinetic phenomenon, selection of material for the relevant experimentations and the parametric studies of the proposed material removal technique will be discussed. Following that, the identification of the material removal mechanism and the proposal of a semi-empirical model will be carried out in chapter 5. Chapter 6 will look accordingly into the application of the electrokinetic material removal technique onto a more commonly used material (aluminium) where the semi-empirical model will be further validated to show its predictive capability. Consequently, chapter 7 will cover the surface roughness analysis on the workpiece after the material removal technique such that the process can be controlled and optimized to precisely remove material while generating a finished surface with predetermined roughness. The conclusion and the future work will be presented in chapter 8.

Chapter 2

Literature review

This chapter reviews the electrokinetic phenomenon as a possible technique for material removal process. With reference to Fig 2.1, the discussion will be divided into five sections. In the first section, the fundamentals of free abrasive machining will be discussed to understand the limitations of the existing technology. This will be followed by section 2.2 on the fundamentals of the electrokinetic processes which will present the various electrokinetic methods that are used currently to manipulate the particles' motion for different applications while section 2.3 will look into the fundamentals of hydrodynamic effects to further understand the trajectory of the particles that are suspended in a fluidic medium. Following that, section 2.4 will briefly discuss about the possible material removal mechanisms that might render material removal in the electrokinetic material removal setup. A summary on the literature outcome will be presented in section 2.5.

Fig 2.1 Overview of Chapter 2

2.1 Fundamentals of free abrasive machining

The fundamentals of free abrasive machining will be covered in this section. This section will first give an insight on the importance and relevance of free abrasive machining. This will be followed by the general definition and mechanism of the process. Subsequently, the issues faced by the technology will be discussed before the evolution of the technology to counteract the problems will be presented.

2.1.1 Importance of free abrasive machining

Abrasive machining techniques are invariantly used in the production of components that require excellent surface finish and high accuracy in material removal with tight tolerances [32]. These techniques are carried out with the usage of abrasive particles either in the form of loose abrasives (polishing, lapping) or bonded abrasives (grinding wheels) for producing components of various shapes, sizes, accuracy, finish and surface integrity [33]. The requirements for the processes range from high resolution, high reliability, high response, high throughput, and high integration for electronic components (VLSI); to high durability, high strength, and high reliability for structural components; to high reflectivity for optical components; to high magnetic permeability for magnetic materials [33]. Usually, the abrasives are obtained in the form of comminution where the fine abrasives are obtained by reducing the size from a larger block of material, which limits the size of abrasives produced [34]. However, manufacturing of ultra-fine particles for better machining capabilities [35,36] are made possible with the advance in technology for the synthesis of these abrasives.

Amongst the abrasive machining methods, free abrasive machining techniques (in the form of loose abrasives), are generally preferred over fixed abrasive machining techniques (in the form of bonded abrasives) during the production of functional devices. This is because free abrasive machining techniques have the higher ability of achieving extremely smooth and possibly damage-free surface without any affected layer or strain [1,25] as compared to the latter. It may be attributed to the fact that the temperature,

average relative speed and concentration of energy in the contact area of the abrasives tend to be lower for free abrasive machining as compared to fixed abrasive machining. Therefore, free abrasive machining processes are one of the few processes that are utilized in high precision finishing to generate surfaces of desired characteristics [37] with surface roughness at the nanometric and even subnanometric region [33]. Furthermore, free abrasive machining is a candidate that has a high potential in achieving excellent machining accuracy at the nanometric level according to the Taniguchi curve (Fig 1.1). One such technique, which falls within free abrasive machining, that is widely used and critical in the manufacturing industry is polishing. In fact, polishing is a key process in the semiconductor industry, in the form of chemical mechanical polishing (CMP) [38-40]. Polishing is also a crucial process for optical products where it is able to generate extremely smooth and defect-free surfaces [41-44]. Moreover, polishing is frequently applied to value-add products by achieving smooth surface textures for aesthetic, durability and other engineering purposes.

2.1.2 General definition and mechanism of free abrasive machining

Free abrasive machining processes utilize a large number of randomly multipointed cutting edges from multiple abrasives for effective material removal at smaller chip sizes as compared to conventional machining processes that use cutting tools with defined edges [45]. The abrasives are usually mixed in a fluid vehicle to form slurry. During the processes, these free abrasives particles are projected onto the surface of the workpiece. The particles are brought into contact with the surface of the workpiece by either direct (e.g. by the presence of the polishing pad and load) or indirect (e.g. by the presence of fluidic pressure and magnetic field [46,47]) mechanical means. The particles can be mechanically brought into contact with the surface of the workpiece by either close-contact (e.g. pitch polishing), semi-contact (e.g. chemical mechanical polishing (CMP)) or non-contact (e.g. float polishing and elastic emission machining) mode [33,48]. Upon projection, the particles may penetrate, roll, indent, slide or scratch across the surface to achieve material removal [49,50] as shown in Fig 2.2 depending on the mode of contact.

Fig 2.2 Schematic showing the behaviour of the particles during free abrasive machining process (a) scratching (b) rolling, sliding and scratching (c) rolling, sliding, colliding and indenting [50]

In free abrasive machining processes for extremely smooth surfaces (e.g. polishing), the semi-contact mode is conventionally used where the material from the surface of the workpiece is detached in a relative motion caused by the protrusion of fixed/free abrasive particles in the slurry between the surfaces of the polishing pad and workpiece as shown in Fig 2.3. The material removal mechanism is termed as a two-body abrasion when the abrasive particles are fixed [37] while the mechanism is termed as a three-body abrasion when the (loose) abrasive particles are free to rotate between the interfacial surfaces [51] during material removal. Due to the differences in the removal mechanism, the two-body abrasion is considered to produce material removal that is three times more than the three-body abrasion under the same loading conditions [52]. Two-body abrasion may occur during polishing when the intended free particles are lodged and fixated onto an external medium (i.e. the polishing pad). As a result, both two-body and three-body abrasions may occur during the process. The dominance of the former or the latter abrasion mechanism depends largely on the polishing conditions during the process.

Fig 2.3 Schematic showing the two body and three body abrasions [37]

During the polishing process, direct chemical actions between the slurry and the workpiece promote the mechanical actions further. By combining different ratios of the chemical and mechanical aspects of the polishing process, various polishing methods have emerged. Fig 2.4 shows the relationship between the polishing mechanisms and the different polishing processes.

Fig 2.4 Relationship between the polishing mechanisms and polishing processes [1]

2.1.3 Issues faced by free abrasive machining

Polishing, a widely used free abrasive machining technique, is utilized to generate material removal with nanometric machining accuracy and surface roughness. The conventional polishing technique involves the use of fine particles in a liquid carrier on a polishing pad. One of the phenomenological material removal models that still remains as a standard reference for polishing is the one that was proposed by Preston [53]. According to the Preston equation, the material removal rate for polishing can be expressed as:

$$\frac{\Delta H}{\Delta t} = K_p \left(\frac{L_d}{A_s} \right) \left(\frac{\Delta s}{\Delta t} \right) \quad (2.1)$$

where $\frac{\Delta H}{\Delta t}$ is the change in the thickness or height (H) over time (t), K_p is the Preston coefficient, L_d is the applied load, A_s is the surface area on which material removal occurs and $\frac{\Delta s}{\Delta t}$ is the relative velocity between the workpiece surface and polishing pad.

Commonly, the Preston equation is rewritten or simplified as:

$$MRR = K_p P_r V_a \quad (2.2)$$

where MRR refers to the material removal rate, P_r is the applied pressure and V_a is the average relative velocity.

The Preston equation was initially proposed for material removal on glass. However, it is realized from literature that the equation can also be extended to other materials such as metallic thin film [54-56].

In conventional polishing, which falls within the close-contact and semi-contact mode, contact of the workpiece, abrasives and polishing pad are involved. With regards to the material removal model proposed by Preston, the polishing load and the relative velocity between the polishing pad with the workpiece are the crucial parameters to the material removal of the process. Although high material removal rate is desired in the polishing process, high material removal rate usually results in high surface roughness. Since conventional polishing methods rely on the presence of polishing pad and load, defects such as microscratches on the surface of the workpiece are inevitably caused. Usually, microscratches are caused by two-body abrasions where the material removal rate for two-body abrasion is much higher than that of the three body abrasion when under the same polishing condition. Two-body abrasion occurs when the unintended fixed abrasives are lodged onto the polishing pad during material removal. Microscratches can be caused by several conditions that includes high polishing load, uneven topography of the polishing pad, irregular abrasive size distribution, agglomeration of abrasives and trapping/lodging of abrasives on polishing pad.

2.1.4 Evolution and technological development of free abrasive machining

Due to the fact that most polishing techniques involve interactions between the polishing pad and workpiece, non-contact polishing approaches (where the machining tool is not in contact with the workpiece [1-4]) have attracted particular interest over recent years. This is because non-contact techniques greatly minimize or eliminate defects such as microscratches that are typically caused by polishing tool and workpiece interaction. Float polishing [2,57], elastic emission machining [3] and field-assisted finishing [58-61] are some of the processes that fall within the non-contact polishing category. All of these techniques utilize slurries, which consist of abrasive particles suspended in fluid, to remove the workpiece material. These processes will be presented in the following subsections.

2.1.4.1 Float polishing

Float polishing is a process that is capable of producing extremely flat surfaces to atomic conformity over large areas [62,63]. The working mechanism relies on the hydroplaning phenomenon of the slurry occurring between the lap/polishing tool and the workpiece [1] that are rotated in simultaneous circular motions as shown in Fig 2.5. For the floating process to work, the interfacial gap must be larger than the diameter of the abrasive particles.

Fig 2.5 A schematic model of float polishing [1]

Due to the relative speed between the lap/polishing tool and the workpiece, a velocity gradient is formed at the interface and the loose abrasive particles within the slurry will sustain driving/shear and normal forces [64] as shown in the schematic in Fig 2.6. These forces, in turn, will result in the reaction force, R , that will act against them. When the resultant force of the driving and normal force is greater than the reaction force, the surface atoms of the workpiece may break bonds with its neighbouring atoms and be removed [64].

Fig 2.6 A schematic showing the forces that are subjected to the abrasive particle in float polishing [64]

However, the float polishing process is usually used as a final step in surface preparation to obtain an extremely flat and smooth surface. This is because when the surface is not smooth enough, the workpiece does not float enough with the hydroplaning effect. When that happens, direct contact of the interfacial surfaces, three-body abrasion and two-body abrasion may occur. This will result in the possibility of multiple micro-scratches occurring and render the float polishing process ineffective. Therefore, the interfacial gap ($\sim 1\text{ }\mu\text{m}$) should always be monitored to be larger than that of the diameter of the abrasive particles ($1\sim 100\text{nm}$) [65] for the process to function properly. Furthermore, the float polishing process requires a machine system, equipped with an ultraprecision hydrostatic-type rotary bearing and a highly accurate air slider, to provide for the flat, mirror-cut tin tool plate as a soft metal tool [1].

2.1.4.2 Elastic emission machining (EEM)

The other non-contact approach to polishing is the elastic emission machining (EEM) technique. When EEM was first demonstrated, the machining setup comprised of a rotating tool, workpiece and slurry as shown in Fig 2.7. During the process, the workpiece and the rotating tool are placed in close proximity (in the order of microns) and are separated by a film of slurry due to the hydrodynamic effect at high rotating speed [66]. The abrasive particles (~100 nm diameter) are much smaller than the film thickness and are carried into the interfacial region by the drag force of the moving fluid. It was proposed that the material removal process is a surface energy phenomenon where each abrasive particle removes a number of atoms from the surface of the workpiece with some probability after coming in contact and chemically reacts with it [3,66-68]. It was also reported theoretically and experimentally that atomic scale fracture can be induced elastically (through EEM) without plastic deformation during the process, to produce ultra-smooth mirror surfaces that are crystallographically and physically undisturbed [3,67].

Fig 2.7 A schematic model of the elastic emission machining [66]

Despite its advantages in achieving atomic material removal, the technique is limited to the small polishing area. Furthermore, the presence of the rotating tool may cause microscratches onto the workpiece if the rotating speed of the tool is not well controlled where the tool is not floating on the surface of the workpiece [66]. To answer to these issues, Yamauchi *et al* [42] improved the technique by introducing the nozzle-head EEM.

Fig 2.8 A schematic model of the nozzle-head EEM [42]

In the nozzle-head EEM, the rotating tool is not present as shown in Fig 2.8. Instead, the ultra fine particles are supplied onto the surface of the workpiece by the flow of the slurry through the nozzle. The improved process relies on the shear flow of the slurry (instead of the drag force generated by the rotating tool in the original proposed technology) to ensure that the bounded abrasive particles on the surface of the workpiece leave to achieve material removal. However, the material removal rate for the nozzle-head EEM ($\sim 18\text{nm/Hr}$) [42] is much slower than that of the rotating tool EEM ($\sim 1\mu\text{m/Hr}$) [3,68].

2.1.4.3 Field assisted finishing

To minimize defects such as microscratches and increase material removal rates of current polishing techniques, field assisted finishing processes are introduced. Usually, field assisted finishing techniques are incorporated to existing methods which result in hybrid finishing processes [69,70]. The fields for field assisted finishing can be in the form of magnetic [46,70,71], electric [72] or both [73]. In addition, field assisted finishing has the attraction for finishing non-planar microstructures where the conventional polishing techniques are incapable of achieving as the polishing pads are larger than the intended machined areas.

2.1.4.3.1 Magnetic field assisted finishing

Magnetic field is used in finishing as a mean of non-contact material removal technique. The abrasive particles are able to be brought into contact with the surface of the workpiece without the presence of the polishing pad and accompanying polishing load. Instead, the abrasives are brought towards the surface of the workpiece through the magnetic properties of the magnetic particles in the slurry. In certain processes, magnetic field has been reported to accelerate the material removal rate of the existing polishing technique [59]. Magnetic abrasive finishing and magnetic float polishing are some examples of magnetic field assisted finishing. Fig 2.9 shows a schematic of the experimental setup for the magnetic abrasive finishing. The surface finish generated by magnetic field assisted finishing is usually in the range of around 50 nm to 100 nm Ra [46,58] although smoother surfaces are also reported [59].

Fig 2.9 A schematic setup of magnetic abrasive finishing [74]

2.1.4.3.2 Electric field assisted finishing

Electric field assisted finishing techniques have been report, over recent years, to be capable of achieving extremely smooth surface roughness at the nanometric range after the material removal processes [72,75-78]. Similarly to magnetic field assisted finishing, electric field assisted finishing does not rely on the polishing pad to drive the abrasive particles onto the surface of the workpiece for material removal. Some of the electric field assisted finishing includes electrorheological finishing and electrolytic abrasive finishing. It was reported by Kuriyagawa *et al* [76] that the presence of the electric field accelerated the material removal rate and, in some way, improved the surface quality of the workpiece as compared to the process without the electric field for electrorheological finishing. Kuriyagawa reported that the material removal efficiency had improved by approximately 6 to 7 times when the material removal was electrorheological fluid-assisted. In electrolytic abrasive finishing, the workpiece is submerged into a sodium nitrate (NaNO_3) solution. The material removal process is made possible by the simultaneous action of electrochemical dissolution on the surface of the workpiece and the abrasive removal of material by the abrasive particles. The principle of electrolytic abrasive finishing is shown in Fig 2.10. The electrolytic abrasive finishing has been reported to produce quality surface finish between 1 nm Ra and 10 nm Ry [79].

Fig 2.10 A schematic showing the principle of electrolytic abrasive finishing [79]

2.1.4.3.3 Magnetic and electric field assisted finishing

Attempts have been made to integrate magnetic and electric fields to assist surface finishing [73,80,81]. When the magnetic and electric fields are present, the fields interact and interfere with one another to enhance the material removal rate as well as the surface finish of the workpiece during the process. One such technique that falls within this category is electrolytic magnetic abrasive finishing [73].

During electrolytic magnetic abrasive finishing, negative electrolytic ions are generated when the electrolyte is subjected to an electrical supply. The negatively charged ions would accelerate towards the workpiece, in a linear path as shown in Fig 2.11, to react with the surface for material removal. With the presence of the magnetic field, the paths of the negative ions are altered to that of a cycloid manner due to the effect of Lorentz' force [81]. This change results in an increase in the material removal rate as well as improved surface finish [73,81]. The rise in the material removal efficiency is attributed to the change in the intensity and direction for the movement of the negative ions which increase the reaction of the ions with the peak points on the surface of the workpiece.

Fig 2.11 Effects of the magnetic field in the electrolytic magnetic abrasive finishing process (a) without magnetic field and (b) with magnetic field [73]

In electrolytic magnetic abrasive finishing, the chemically-reacted workpiece is easier to be removed as compared to the original metal surface. This accounts for the faster material removal rate of the electrolytic magnetic abrasive finishing as compared to magnetic abrasive finishing.

2.1.5 Concluding remarks on free abrasive machining

Free abrasive machining is an attractive mean of achieving nanometric material removal with a very smooth surface. When an extremely smooth surface with preferably no defect is desired, polishing is one of the techniques within free abrasive machining to achieve it. This is especially so when the requirements for the surface finish overwhelm the form accuracy of the workpiece. However, conventional polishing processes usually come together with the presence of polishing pads and accompanying polishing loads. The presence of the polishing pads and loads bring about the possibility of defects such as microscratches. Therefore, non-contact polishing techniques are desired to counter these issues. These non-contact polishing techniques are summarized in Table 2.1.

Table 2.1 A comparison of polishing processes

Machining technique	Advantages	Limitations
Conventional polishing	<ul style="list-style-type: none">• Able to produce planarized and flat surfaces	<ul style="list-style-type: none">• Contact process• Machining load from the polishing pad causes defects such as microscratches
Float polishing	<ul style="list-style-type: none">• Non-contact process• Able to produce planarized and flat surfaces• Atomic material removal process• Chemical used is non-toxic	<ul style="list-style-type: none">• Requires the workpiece surface to be smooth before machining [1]• Requires a high precision technology to mount the polishing tool at a particular distance from the workpiece• Rotating tool has to rotate above a certain speed to achieve the non-contact polishing condition [64]
Elastic emission machining (Rotating tool type)	<ul style="list-style-type: none">• Non-contact process• Atomic material removal process• Chemical used is non-toxic	<ul style="list-style-type: none">• Requires a high precision technology to mount the rotating tool during material removal process [3]• Rotating tool has to rotate above a certain speed to achieve the non-contact polishing condition [66]
Elastic emission machining (Nozzle-head type)	<ul style="list-style-type: none">• Non-contact process• Atomic material removal process• Chemical used is non-toxic	<ul style="list-style-type: none">• Requires a high precision technology to mount the workpiece during material removal process [82]• A very slow process [42] (as slow as 1nm/Hr)
Magnetic field assisted finishing	<ul style="list-style-type: none">• Non-contact process• Chemical used is usually non-toxic	<ul style="list-style-type: none">• The surface finish is usually in the range of around 50nm to 100nm Ra [46,58]
Electric field assisted finishing	<ul style="list-style-type: none">• Non-contact process• Quality surface finish between 1nm Ra and 10nm Ry has been achieved in electrolytic abrasive finishing [79]	<ul style="list-style-type: none">• Utilizes chemical reaction for material removal• Chemical used is rather toxic
Electric and magnetic field assisted finishing	<ul style="list-style-type: none">• Non-contact process• Quality surface finish has been achieved in electrolytic magnetic abrasive finishing [73]	<ul style="list-style-type: none">• Utilizes chemical reaction for material removal• Chemical used is rather toxic

Ultimately, to realize atomic-size machining, new phenomenon distinct from the conventional processes can be developed to achieve it. Several interesting non-contact polishing techniques were discussed. Amongst the few techniques, elastic emission machining appears to be a very attractive option to attain an extremely smooth and defect-free surface with atomic machining accuracy. However, elastic emission machining has its limitation in the two modes of operation (i.e. rotating tool and nozzle-head type). The rotating tool type EEM is hindered by the rotating tool while the nozzle-head type EEM is restricted by the extremely slow material removal process. Between the two EEM processes, the nozzle-head type EEM seemed to be more attractive if the material removal rate can be improved as the latter does not involve the presence of the polishing pad during material removal.

Due to the limitations of the current atomic-size machining methods, new machining techniques are sought and developed to add as alternative processes to the current ones. A field assisted material removal method that utilizes the EEM concept can be developed as an alternative to the current nanometric material removal techniques where it is reported that both electric and magnetic field can enhance the material removal rates of the processes. This is due to the increase in the participation of the abrasive particles on the surface of the workpiece for faster material removal [70,76,83]. Due to the ease of particle control by electric field [84,85], an electric field assisted technique for atomic material removal is proposed and should be carried out to look at the feasibility of adopting such technique for material removal - material removal utilizing electrokinetic phenomenon (a.k.a electrokinetic material removal process).

2.2 Fundamentals of electrokinetic effects

A brief description of electrokinetic effects will be covered in this section. This section will first introduce the electrokinetic effects that are utilized for different applications in the various industries. This will be followed by the theory of some of the commonly used electrokinetic effects that may be applicable in the control of particles for possible material removal.

2.2.1 Electrokinetic (EK) methods and applications

Over recent decades, electrokinetic mechanisms have been broadly used to manipulate the motion of particles and fluids in fluidic systems [31,86-88]. Electrokinetic phenomena can be defined as the manifestations of electrical properties of interfaces that involve tangential fluid motion adjacent to a charged surface [89]. In the studies of particles in a microchannel, it is usually concerned with the movement and the behaviour of particles in suspension when they are subjected to electrical fields [87]. Basically, electrokinetic phenomena are divided into two major groups that are known as direct current (DC) electrokinetic effect and alternating current (AC) electrokinetic effect [21,88].

DC electrokinetic effect is termed as the effect of the particles/fluid (motion) under the influence of DC electric field. The effect can be further classified into several different techniques. Amongst these different techniques, the four more commonly used ones are electrophoresis, electroosmosis, streaming potential and sedimental potential [88,89].

On the other hand, AC electrokinetic effect refers to the manipulation of the particles' motion when they are subjected to AC electric field [87]. Likewise, the AC electrokinetic effect can be classified into several different techniques. Amongst these techniques, the two more commonly used techniques are dielectrophoresis and electrorotation [21,88].

Electrokinetic phenomena play a large role in several industrial processes, water treatment and biological functions. In the industrial processes, the electrophoretic phenomenon is used to extract/separate mineral from mixtures, while electroosmosis is used in water treatment as a soil dewatering tool close to contaminated sites. In terms of biological functions, there has been great emphasis on using electrokinetic phenomena with the introduction of microfluidics for micro total analysis systems (μ TAS) [86]. In μ TAS, electrokinetic effects are mainly used for the separation of particles/cells. Some of the more commonly used effects for μ TAS are electrophoresis [90] and dielectrophoresis [28,87].

2.2.2 Theory of electrokinetic effects

As mentioned in section 2.2.1, there are several electrokinetic phenomena that are widely used for various applications. However, only the electroosmotic, electrophoretic and the dielectrophoretic effects would be discussed as they appear to be the most relevant electrokinetic phenomena that would drive the particles to collide onto the workpiece with a certain impact that is high enough to cause atomic level material removal. Electrostatics will be briefly introduced before the electrokinetic effects are discussed as electrostatic phenomenon is closely related to the electrokinetic effect in the fluid.

2.2.2.1 Electrostatic

Electrostatic is the build-up of charges on the surface of an object when it is in contact with other surfaces. One such example in the context of microfluidics is the electric double layer that is formed when a particle is submerged in the fluidic medium.

When a particle is submerged in an aqueous solution, it is charged as the solid surfaces of the particle carry electrostatic charges where a difference in potential is developed across the interface between the two phases. The charged interface of the particle will attract counter-ions and repel co-ions to form an electric double layer (EDL) [91] as shown in Fig 2.12.

Fig 2.12 (a) A schematic showing the electric double layer according to Stern's model (b) The potential distribution of the electric double layer

The EDL model was developed by Gouy and Chapman in the early 1910s and was improved by Stern in 1924. According to the EDL model, the EDL consists of two layers: the compact and diffuse layers [92]. The compact layer usually lies next to the solid immediately where the counter-ions of the liquid are strongly attracted to the solid surface making the counter-ions there immobile. The compact layer is approximately one hydrated ion radius and is confined within the Stern plane which carries the Stern potential (ψ_s). On the other hand, the diffuse layer is the layer from the compact layer (starting from the shear plane) to the uniform bulk liquid and the ions are mobile in this

region. Usually, the shear plane layer is approximately one to two radii away from the solid surface and is also referred as the no-slip fluid flow boundary. The potential at the shear plane is known as the zeta potential and is only marginally different in magnitude from the Stern potential. The zeta potential characterizes the strength of the EDL and is a determining factor for all electrokinetic phenomena.

The EDL thickness is sometimes referred as the Debye length (κ^{-1}) and the expression [93] for κ^{-1} is given by the formula:

$$\kappa^{-1} = \left[\frac{\epsilon_r \epsilon_0 k_b T_o}{2z^2 e^2 n_\infty} \right]^{\frac{1}{2}} \quad (2.3)$$

where ϵ_r is the relative dielectric constant, ϵ_0 is the permittivity of free space, k_b is the Boltzmann constant, T_o is the temperature, z is the valency of the ions, e is the fundamental electric charge and n_∞ is the ionic number concentration in the bulk solution.

2.2.2.2 Electroosmosis

Electroosmosis is the movement of electrolyte relative to a charged stationary surface under the influence of an external electric field. It is the resultant of the force on the counter-ions of the liquid (the mobile part of the diffuse double layer) exerted by the electric field that causes it to move within the charged object (capillaries, pores, etc) [94]. The electroosmotic phenomenon is illustrated in Fig 2.13.

Fig 2.13 A schematic showing electroosmosis phenomenon (A) An electric double layer in the electrolyte is formed as a result of the negatively charged wall (B) The cations in the diffuse layer causes a net electroosmotic flow in the direction of the cathode when the electric field is applied. (C) Electroosmotic velocity profile is uniform in the cross section of the capillary [21]

Two of the more relevant expressions that represent the electroosmotic phenomenon are the electroosmosis velocity and mobility equations.

The electroosmotic velocity equation is given by [95]:

$$v_{EOF} = \mu_{EOF} E \quad (2.4)$$

where μ_{EOF} is the electroosmotic mobility and E is the applied electrical field

To determine the electroosmosis velocity, the electroosmotic mobility has to be determined first, by using the formula:

$$\mu_{EOF} = \frac{\varepsilon\zeta}{\eta} \quad (2.5)$$

where ε is the dielectric constant, ζ is the zeta potential and η is the fluid viscosity

2.2.2.3 Electrophoresis

Electrophoresis is the migration of ions/particles in a fluidic medium under the influence of electric field. As mentioned in section 2.2.2.1, when the particles are submerged in aqueous solution, the solid surfaces carry electrostatic charges. The surface charges of the spherical particles are related to the particle's zeta potential and size which can be determined by the expression [88]:

$$Q_E = 4\pi\varepsilon_r\varepsilon_0r(1+\kappa.r)\zeta \quad (2.6)$$

where Q_E is the surface charge of the colloidal particle, r is the radius of the particle, ε_r is the relative permittivity, ε_0 is the permittivity of vacuum, and ζ is the zeta potential of the particle.

The electrophoretic force that acts on the particle due to the influence of an external electric field can be expressed by the following equation:

$$\begin{aligned} F_E &= Q_E E \\ F_E &= [4\pi\varepsilon_r\varepsilon_0r(1+\kappa.r)\zeta] E \end{aligned} \quad (2.7)$$

where E is the external electric field that is acting on the spherical particle

2.2.2.4 Dielectrophoresis (DEP)

The term dielectrophoresis (DEP) was introduced by Pohl in 1951 to describe the motion of particles that are caused by the dielectric polarisation under the influence of non-uniform electric fields [96]. Dielectrophoresis is usually based on AC electric field. However, dielectrophoresis based on DC electric field was later introduced in 1978 by Jones [97]. When subjected to an AC field, the dielectric permittivities of the materials become a complex function and are given by:

$$\varepsilon^* = \varepsilon - i \frac{\sigma}{\omega} \quad (2.8)$$

where ε^* is the complex electrical permittivity, ε is the real part of the electrical permittivity, σ is the electrical conductivity and ω is the frequency of the AC field signal

When a particle is more polarized than the fluidic medium, the DEP force pushes the particle towards the region of higher electric field and is known as a positive DEP. On the other hand, when the medium is more polarized than the particle, the particle would be driven towards the region of lower field strength and is referred as a negative DEP. DEP causes motion due to the polarization of material and the DEP force that the particle is subjected to, in a non-uniform electric field, is given by [98]:

$$F_{DEP} = 2\pi r^3 \varepsilon_m \operatorname{Re}[f_{CM}] \nabla \left| \vec{E} \right|^2 \quad (2.9)$$

where r is the radius of the spherical particle, ε_m is the real part of the complex permittivity of the medium, f_{CM} is the Clausius Mossotti factor, $\operatorname{Re}[f_{CM}]$ is the real part

of f_{CM} and $\nabla \left| \vec{E} \right|^2$ is the gradient of the square of the electric field quantifying the non-uniformity of the electric field.

The Clausius Mossitti factor gives the frequency dependence of the polarization effect and is expressed by:

$$f_{CM} = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*} \quad (2.10)$$

where ε_p^* is the complex electrical permittivity of the particle and ε_m^* is the complex electrical permittivity of the medium

2.3 Fundamentals of hydrodynamic effects

Fluid dynamics is the study of fluid when it is in motion. To understand the behaviour of a particle within a fluidic medium, several theories and equations from the study of hydrodynamic effects have to be considered. In this section, Stokes' law (sometimes regarded as drag force) and volumetric flow rate will be specifically introduced.

2.3.1 Stokes' Law (Drag force)

When a particle is in a motion within a fluidic medium, it is normally retarded by a frictional force. The frictional force that exerts onto these particles, which moves through the fluid with low Reynolds number, is referred as the drag force and can be given by the expression [99]:

$$F_{Drag} = C_D \left(\frac{dy}{dt} \right) \quad (2.11)$$

where C_D is the frictional coefficient and $\left(\frac{dy}{dt} \right)$ is the particle's speed

When a small spherical particle is assumed, the frictional coefficient becomes:

$$C_D = 6\pi\eta r \quad (2.12)$$

where η is the viscosity of the fluid and r refers to the radius of the particle

Furthermore, when the particles are in close proximity to large solid walls (as compared to the particles), the presence of the wall will have a considerable effect on the drag force as well. The presence of the wall boundary at a finite distance necessitates a modification to the Stokes' law by multiplying a dimensionless correction factor, $\alpha(h)$, such that the equation becomes [99-102]:

$$F_D = [\alpha(h)](6\pi\eta r) \left(\frac{dy}{dt} \right) \quad (2.13)$$

and

$$\alpha(h) = \frac{6h^2 + 9rh + 2r^2}{6h^2 + 2rh} \quad (2.14)$$

where h is the instantaneous thickness of the gap between the planar wall surface and the closest point on the particle

2.3.2 Volumetric flow rate

The volumetric flow rate is referred to the rate of flow of fluid in a fluidic channel. It is usually represented by Q and is the product of the fluidic velocity and channel cross sectional area [103]:

$$Q = AU \quad (2.15)$$

where A is the cross sectional area of the channel and U is the general velocity of the fluid

2.4 Fundamentals of material removal mechanisms

There are presently several methods to model the free abrasive machining material removal phenomenon. In this report, only the more common and relevant material removal mechanisms would be discussed. The material removal models that are introduced in this section will be classified into i) mechanical and ii) non-mechanical material removal mechanisms. The mechanical material removal mechanisms would consist of a) the atomic layer removal model in elastic emission machining and b) the erosion model pioneered by Finnie [104]. On the other hand, the non-mechanical material removal model would consist of 1) chemical dissolution 2) electrochemical corrosion [105,106] and electro machining [107].

2.4.1 Mechanical material removal mechanisms

In the mechanical material removal mechanisms, the elastic emission machining and the erosion model will be discussed. These two models would be discussed only as they are the most relevant models that would be used in the proposed material removal technique in the research, i.e., Electrokinetic material removal.

2.4.1.1 Atomic material removal model in elastic emission machining

It was concluded in section 2.1 that elastic emission machining (EEM) posed as a very attractive means of achieving atomic material removal with a possibly defect-free surface. In one way, EEM can be regarded as a mechanical material removal technique. A brief introduction of the machining setup was earlier mentioned in section 2.1.4.2. This section strives to go into a more detailed depth in understanding the principle of the material removal mechanism to complement with the earlier section.

In 1987, Mori [3] suggested a material removal mechanism for EEM and even mentioned in his later years that his suggested material mechanism might apparently be evident in the float polishing process [64].

The EEM method makes use of the hydrodynamic effect to achieve a thin film of fluid between the workpiece and the rotating tool as shown previously in Fig 2.7. The fluid film is approximately $1\text{ }\mu\text{m}$ as compared to the abrasive particles (silicon oxide) of 100 nm which are much smaller. The abrasive particles in the slurry are transported into the region between the rotating tool and the workpiece by the drag force of the moving fluid. As the abrasive particles are embodied with a considerable amount of velocity upon collision onto the surface of the workpiece, atomic material removal is formed by means of elastic fracture.

Elastic fracture of the order of atomic size can be made possible by colliding fine abrasive particles onto the workpiece. As long as the excessive energy is not transmitted beyond the targeted atoms by the colliding abrasive particles, a very smooth surface finish can be obtained. It was suggested that the most appropriate criteria for EEM to take place was when the conditions for the removal of the atoms from the workpiece agreed with that of machining. This is such that little energy is imparted beyond the targeted atoms which may perturb the atomic structure of the workpiece surface. Therefore, the energy that is supplied to the abrasive particles for material removal, on collision with the workpiece, has to be precisely controlled to further enhance the EEM process.

Mori proposed that the EEM material removal process can be assisted by the interaction generated in the interface between the abrasive particles and the workpiece.

When a silicon oxide particle is submerged into aqueous solution, the siloxane groups (Si-O-Si) are hydroxylated into silanol groups (Si-OH) and silicic acid groups (Si-O^-) [108,109] as shown in Fig 2.14.

Fig 2.14 The three main groups of the silicon oxide surfaces which can be reversibly interchanged with the additional and removal of water [108]

As the particle approaches the surface of the workpiece, interactions between the two surfaces occur where the particles and the atoms of the workpiece are bonded together ionically as shown in Fig 2.15.

Fig 2.15 Interactions between an abrasive particle and the surface of the workpiece. (a) Surface structures before interaction (b) Hydrogen bonding between two surfaces (c) Interface structure (d) Separation of adsorbed particle with work atom removals [67]

As the particle moves away from the surface of the workpiece by the drag force of the fluid, the atoms from the workpiece are removed as shown in Fig 2.15 (d). It was reported that the metallic inter-atomic bonds are weaker as compared to the stronger ionic bonds that are formed during the surface interaction of the two medium. As a result, there is a higher tendency for the metallic inter-atomic bonds to be broken before the ionic

bonds between the two medium were broken. This leads to the removal of the material from the workpiece in an atomic fashion [67]. During the removal mechanism, the drag force of the fluid has to be large enough to move the bounded particle away from the workpiece or else, no material will be removed away from the workpiece. This drag force is derived from the shear stress action of the fluid where it is a function of the lubricating condition of the slurry [66].

It was reported by Su *et al* that the lubrication condition of the slurry can be divided into three regimes as shown in Fig 2.16, namely:

- *Isoviscous-rigid (IR) regime*. In this regime, the elastic deformation (of the rotating tool with the surface of the workpiece) is negligible as compared to the film thickness
- *Isoviscous-elastic (IE) regime*. In this regime, the elastic deformation (of the rotating tool with the surface of the workpiece) is significant and the viscosity increment is negligible
- *Viscous-elastic (VE) regime*. In this regime, both the elastic deformation (of the rotating tool with the surface of the workpiece) and viscosity increment are significant

Fig 2.16 Schematic diagram of lubrication regimes, associated with the applied load and tool speed [66]

Su *et al* reported that the material removal rate for the various regime followed different trends as the shear stress for the regimes are different. They modelled the shear stress curves as shown in Fig 2.17 and showed that there were close relationships between their model and the experimental data.

Fig 2.17 Quantitative trends of shear stress ratio τ_{speed} and machining rate ratio M_{speed} under the variation of tool speed [66]

Su reported that the lubrication condition usually falls within the IR and IE regimes during polishing process due to the polishing and lubrication conditions as shown in Fig 2.18.

Fig 2.18 Schematic diagram of material removal rate vs relative speed or slurry viscosity in a lubricating range covering IE and IR lubrication regimes [64]

To model the material removal rate of EEM, Su *et al* associated the material removal rate with that of the shear stress of the slurry flow [4,64,66]:

$$MRR \propto \frac{1}{\gamma} \cdot G(\tau_{slurry}) \quad (2.16)$$

where MRR is the material removal rate, γ is the surface energy of the workpiece that has to be overcome for material removal to occur, G is an increasing function and τ_{slurry} is the shear stress of the slurry flow.

Su [64] suggested that the Preston equation is relevant in describing the material removal process when the free abrasive processes are in the IE lubrication regime. However, when the material removal falls within the IR regime, the Preston model does not apply. When the material removal falls within the IR regime, it was experimentally determined that

material removal was proportional to the polishing load but inversely proportional to the relative speed of the polishing pad [66,110]. Su [66] accounted the difference in the material removal trend due to the disparity in the lubrication regime and utilized an equation under the IR lubrication regime to model the material removal rate.

On the other hand, Kanaoka *et al* and Kim *et al* [110,111] accounted the difference in the material removal trend to the particle concentration. Kanaoka continued to use the Preston equation to model the material removal with the consideration of the particle supply between the workpiece and the rotating tool during the material removal process.

2.4.1.2 Erosion model

Erosion occurs when abrasive particles, entrained in a fluid stream, strikes onto a surface to achieve material removal on it. The material removal mechanism is caused by the inertia of the abrasive particles that is empowered by the hydrodynamic force of the moving fluid. It was realized that the material removal rate of the erosion process varied with changing impingement angles (as shown in Fig 2.19) of the abrasive particles.

Fig 2.19 A schematic to show particle impingement

In 1960, Finnie introduced a modelling equation that could account for material removal for erosion processes [104,112-115]. He related the material removal of the erosion process with the kinetic energy and angle of impingement of the particles:

$$V_0 = Cf(\alpha_p) \frac{m_p V_p^n}{\sigma} \quad (2.17)$$

where C is a constant that is related to the amount of the particles impacting on the surface of the workpiece, V_0 is the volume of the material removal, α_p is the angle of impingement, m_p is the mass of the eroding particle, V_p is the velocity of the particle, n is an exponential value (in the region where $n \approx 2$) and σ is the flow stress.

In his work, Finnie emphasized that the angle of impingement of the particles substantially affects the material removal rate of the material. He reported and performed research on several types of workpieces and abrasive materials for erosion processes [104,116]. In general, the material removal rate of the ductile workpieces followed the same trend. Fig 2.20 shows the typical graph between the relationship of the angle of impingement of the particles and the material removal rate of the ductile workpiece.

Fig 2.20 The influence of the angle of impingement of the abrasive particles on the material removal rate of the ductile workpiece [104]

Finnie observed that the optimal angle of impingement of the particles occurs between 15° and 20° for metallic material while the angle of impingement for the hard and brittle material can range from grazing angle to angle of impingement of 90° . This is shown in Fig 2.21.

Fig 2.21 The optimal angle of impingement of the abrasive particles on different workpiece materials [117]

The large variation in the abrasive angle of impingement for the brittle material largely depends on the size and type of particles that was used during the material removal process. When the particles are very small, the workpieces are removed in the ductile mode while the material removal mechanism that is caused by the large abrasive particles proved otherwise as shown in Fig 2.22.

A strong dependence on the angle of impingement of the abrasive particles is observed in the Finnie model which further emphasizes the relationship between the angle of impingement and the material removal rate of the process.

Fig 2.22 The relationship between the size of the abrasive particles and the optimal angle of impingement for maximum material removal rate of the workpieces [117]

Studies on different material workpieces and abrasive particles were also made for the erosion studies. Finnie experimented on a similar workpiece with different abrasive particles and concluded that the different types of particles gave comparable erosion trend with the conditions that the particles do not fracture during cutting. This observation was reported by other investigators as well [118] as shown in Fig 2.23.

Fig 2.23 The relationship between the types of the abrasive particles and material removal rate of similar workpiece [118]

Finnie also studied the erosion of different ductile materials with similar particles and observed that the angle of impingement fell in the range of 10° to 20° (for optimal material removal) with different volumes of material removal as shown in Fig 2.24.

Fig 2.24 Erosion of aluminium, gold and magnesium with abrasive particles [117]

In his later reports [112,114,119], Finnie continued to build on his model and suggested that the material removal rate at a certain impingement angle to be optimal due to the motion of the contacting tip of the particles upon impingement with the surface of the workpiece, $\dot{x}_t'$. The velocity of the contacting tip of the particle is denoted as [112]:

$$\dot{x}_t' = V_p \cos \alpha_p - \frac{2V_p (1 + m_p r^2 / I_p)}{K} \sin \alpha_p \quad (2.18)$$

and
$$I_p = \frac{m_p r^2}{3} \quad (2.19)$$

where r is the radius of the particle, I_p is the moment of inertia of the particle about its centre of gravity and K is the ratio of the vertical to the horizontal force components acting on the impacting particle

He postulated that for low values of α_p , the particle may leave the surface of the workpiece after impingement. However, when at high values of α_p , the particle is suggested to dwell on the surface which causes the value of $\dot{x}_t'$ to approach zero. With the implementation of $\dot{x}_t'$, the resulting prediction model for the erosion process on material removal becomes

$$V_0 = \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p}\right)} \cdot \frac{2}{P} \left[\sin 2\alpha_p - 2 \frac{\sin^2 \alpha_p}{P} \right], \quad \alpha_p \leq \hat{\alpha}_p \quad (2.20)$$

$$V_0 = \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p}\right)} \left[\cos^2 \alpha_p \right], \quad \alpha_p \geq \hat{\alpha}_p \quad (2.21)$$

$$\hat{\alpha}_p = \tan^{-1}\left(\frac{P}{2}\right) \quad (2.22)$$

and

$$P = \frac{K}{1 + \frac{m_p r^2}{I_p}} \quad (2.23)$$

where p (which is related to hardness) is the flow pressure between the abrasive and the surface of the workpiece, $\hat{\alpha}_p$ is the angle of impingement for maximum material removal and P is a constant that is related to the coefficient of friction between the abrasive particles and the surface of the workpiece

The Finnie erosion model holds true for generally all process related material removal with several assumptions made:

- Material is removed only by the abrasive particles that meets the criteria in material removal
- The particle is rigid and does not fracture during the process
- Rotation of the particles is small during the material removal process
- The abrasive particles do not rebound upon the initial collision with the surface of the workpiece, i.e. the abrasive particles do not collide with the surface of the workpiece again after initial impingement

2.4.2 Non-mechanical material removal mechanisms

In this section, non-mechanical material removal mechanism would be discussed. The section will cover all the possible non-mechanical material removal mechanisms that might be present during the proposed material removal process. The material mechanisms would be categorized into two parts, namely, 1) chemical dissolution and 2) electrochemical corrosion and electro machining.

2.4.2.1 Chemical dissolution

When a material is engulfed in a chemical environment, chemical reactions might take place. Material is removed from the workpiece by controlled chemical dissolution when it is in contact with a strong chemical reagent, i.e. etchant. Etchants can be acidic or alkaline solutions maintained within a controlled chemical composition and temperature for chemical dissolution on the intended surface of the workpiece. During chemical reactions, the atoms at the surface of the workpiece react with the environment around it. Usually, a material (such as metal) is removed away by exposing it in a chemical fluid where the anions will react with the metallic surface to form a compound [25]. The compound is usually either gaseous, aqueous or in liquid form which renders material removal from the metallic surface when the material is removed from the solution.

2.4.2.2 Electrochemical corrosion and electro machining

Electrochemistry is the study of the chemical reactions that take place in a fluid at the interface of the electrodes when a voltage potential is supplied to them [25]. Some of the daily applications for this process include electroplating and electrolysis. Conversely, corrosion refers to the attack on the material through reactions with the surrounding medium. As such, electrochemical corrosion refers to the study on the attack of the material due to chemical reactions under the influence of an electric field. Electro machining refers to the study of using electrical field to perform machining.

Electrochemical corrosion can be classified under two main categories, namely general corrosion and localized corrosion [120,121]. General corrosion is the case when the exposed metal is entirely corroded while localized corrosion refers to the non-uniform corrosion of metal when voltage potential is supplied to the electrodes [106]. Some of the more likely unintended electrochemical corrosions that might take place in the electrokinetic material removal phenomenon will be discussed in this section.

2.4.2.2.1 Galvanic corrosion (Uniform corrosion)

Galvanic corrosion is an electrochemical process when the metallic surface of the anode corrodes in an electrolyte solution [120]. When two or more different metals come into contact in the presence of an electrolyte, a galvanic couple is set up as different metals have different electrode potentials. The electrolyte provides a means for ion migration whereby metallic ions can move from the anode to the cathode. This leads to the anodic metal corroding more quickly than it otherwise would. The presence of electrolyte or a conducting path between the metals may cause corrosion where otherwise neither metal alone would have corroded. Usually, the galvanic corrosion is generally uniform. However, if a dielectric fluid is used, it will only form an electric path when it breaks down. This might give rise for pitting to occur.

2.4.2.2.2 Pitting corrosion (Localized corrosion)

Pitting is a localized attack that occurs generally with the presence of dielectrics due to the stimulation of the anode reaction by activating anions and of the cathode reaction by the presence of oxidizing agents [121]. In order for a pitting attack to occur on a metal, a certain corrosion potential (pitting or breakdown potential) must be attained. A pit is initiated by the adsorption of activating anions on the defective sites in the dielectric. When the pitting potential is attained, the electric field strength above the thinnest parts of the dielectric will be so high that the anions will penetrate the film and a subsequent local dissolution of the metal surface might occur. Some of the other common causes that can initiate the pitting process might be due to coating failure, mechanical discontinuities and microstructural phase heterogeneities.

2.4.2.2.3 Electrical arcing (Localized corrosion)

Electrical arcing refers to the breakdown of fluid due to high voltage potentials between the electrodes [122]. Due to the high electric strength between the local peaks of the electrodes, a plasma channel is formed where the anions generate a substantial amount of heat which vaporizes the dielectric fluid around the plasma channel and causes the formation of a gas bubble. Owing to the high temperature generated during the

vaporization (between the range of 4000K to 10 000K [123,124]) the heat flux of the plasma also melts away the surface of the electrodes.

In the case of the spark discharge that is used in electrical discharge machining (EDM), the plasma channel begins to discharge and the gas bubble implodes once the applied voltage is removed with the current flow ceased. With the plasma channel collapsing, the pressure within it drops rapidly. This results in an implosive force in the gas bubble which causes the molten part of the electrodes to be expelled through the gas bubble and the dielectric fluid. So far, the smallest feature that has been machined using the EDM method has been approximately 1 μm [125]. The process for the EDM process is shown in Fig 2.25. However, there have been several reports that mention that a similar machining technique, known as nanoscale electro machining is able to machine smaller features.

Fig 2.25 EDM process (a) High electric field intensity at the local peaks of the electrodes. (b) Gas bubble and plasma channel formation (c) Imploding of gas bubble when plasma channel collapses (d) Material is removed from both electrodes

2.4.2.2.4 Electro machining (*Localized corrosion*)

Malshe *et al* [126-128] reported that electro machining is able to achieve nanometric material removal. The experimental setup that was performed was similar to the one from EDM except that the electrode is placed extremely near to the metal workpiece (1~2 nm). Malshe *et al* reported the electro machining process as nanoscale electric discharge driven machining (nano-EDM). It was reported that the machining mechanism was due to the electric field assisted trapping and localized assembly of the dielectric molecules between the electrode and the metal workpiece by resonant tunnelling. Malshe *et al* suggested that the resonant tunnelling, that occurs through the transferring of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) under the influence of a threshold voltage, provides the energy for the material removal process and related it to quantum mechanics. They reported that the energy required for material removal is a function of applied bias and current.

2.4.2.2.5 Stress corrosion cracking (*Localized corrosion*)

When a composite of multi-layered material is subjected to a tensile and corrosive environment, the material can fail prematurely below the yield strength [106]. If the material fail as a result of hydrogen embrittlement due to the hydrogen atoms during the manufacturing process, the phenomenon can be classified as hydrogen-induced cracking (HIC) [105,129]. The HIC phenomenon occurs due to the formation of the hydrogen molecules within the internal cavities of the composite material. When the hydrogen molecules are formed, they cause immense pressure in the interface of the metallic layers which may lead to blister formation. The HIC phenomenon can be catalyzed by introducing high temperature or voltage potential to the composite material.

2.4.3 Overview of material removal mechanisms

In this section, descriptions of the various possible material removal mechanisms were discussed. The possible material removal mechanisms were categorized into mechanical and non-mechanical ones. The discussed mechanical mechanisms comprised of atomic

material removal in elastic emission machining, erosion material removal model, chemical dissolution and electrochemical material removal. In order to control the material removal of the electrokinetic technique, an understanding of the material removal mechanisms has to be carried out. It was discussed that the workpiece material could be removed mechanically if the mechanical action (kinetic energy) of the abrasives were larger than the inter-atomic bonds between the metallic atoms of the workpiece. Furthermore, other non-mechanical methods (such as chemical dissolution and electrochemical corrossions) which might cause material removal on the workpiece were also mentioned. A well-structured experimental design had to be considered in order to quantify the various material removal mechanisms.

2.5 Outcome of the literature review

This chapter has given an overview on the fundamentals of the free abrasive technologies that are currently available and applied in industry. A brief discussion of the various free abrasive machining techniques was presented. Comparisons between these techniques were also made to understand the limitations of these machining methods. Amongst the free abrasive machining techniques, it was realized that the nozzle-head type elastic emission machining (EEM) technique holds the greatest attraction of achieving atomic material removal with an extremely smooth surface and possibly the least defects. In EEM, material is removed from the workpiece in the atomistic manner through elastic fracture in the order of atomic size. However, the main issue is that the material removal rate for this process is extremely slow (as slow as 1 nm/HR). As it has been reported that the presence of an assisted field can increase the material removal rate of the process, an alternative method of impinging the abrasive particles onto the surface of the material by utilizing electrokinetic phenomenon with possibly the same concept of EEM is proposed. The electrokinetic phenomenon is proposed as the manipulation of particles in electric field is well-established. This makes it possible to project the abrasive particles in the slurries with a certain impact velocity to collide with the workpiece to achieve nanometric material removal, in approximately the same manner as EEM. The EEM

approach also holds the attraction of being one of the least toxic and cheapest methods to produce nanometric structure.

To manipulate the behaviour of the abrasive particles in the dielectric fluid, the electrokinetic phenomenon was introduced where a range of the various electrokinetic effects were discussed. Hydrodynamic effect was also introduced to further understand the motion of the particles under the dynamics of the fluid flow.

To understand the material removal of the workpiece, different mechanisms were studied. These studies were necessary to identify the prominent material removal mechanism(s) of the workpiece and to determine the relationship of the various parameters of the electrokinetic technique with respect to the material removal rates.

Consequently, the outcome of the literature review provided the following contributions respectively:

- To recognize the need to introduce a new technique to achieve nanometric material removal
- To understand the feasibility of using electrokinetic phenomenon and hydrodynamic effects for the manipulation of the abrasive particles
- To identify and study the various parameters that might influence the behaviour of the abrasive particles
- To identify and realize the various mechanisms that can account for the material removal rate of the electrokinetic material removal technique

Chapter 3

Experimental methodology and characterization techniques

The literature review revealed electrokinetic phenomenon as a possible method for material removal process. However, due to the absence of experimental work in this area, the feasibility of achieving material removal by utilizing this technique is unclear. Thus, initial experimentation should be carried out to provide evidence that the phenomenon is possible in achieving material removal before parametric studies can be undertaken.

This chapter will cover the experimental methodology which includes the experimental setup, equipments and experimental procedures used. The chapter also includes the different characterization techniques that are carried out to observe the machining features.

With reference to Fig 3.1, this chapter will be divided into three sections. Section 3.1 will discuss about the experimental setup of the electrokinetic material removal experiment while section 3.2 will discuss about the characterization techniques that were used to observe the machining features. Subsequently, a chapter summary will be included.

Fig 3.1 Overview of Chapter 3

3.1 Details on electrokinetic material removal study

A test structure was designed to perform the electrokinetic material removal experiment. The structure was fabricated in a manner such that it could allow the different parameters, which would affect the material removal of the workpiece, to be studied during the experiment. The structure consisted of a channel between the electrode and the workpiece, where fluid can pass through. Subsequently, slurry and electrical voltage were

supplied to the test structure. Characterization of the workpiece was then made to determine the material removal and the likely material removal mechanism.

Two different sets of experiments were conducted using the test structure. One set of experiments was for the flow visualization and particle movement under the influence of electric field while the other set of the experiments was for the material removal of the workpiece.

3.1.1 Experimental setup

Fig 3.2 Schematic of the test structure

The structure of the experimental setup is shown in Fig 3.2. The test structure consisted of a workpiece and a base substrate with a thin film of material forming a channel between the both of them. During the fabrication, a layer of silicon dioxide (1 μm) was grown on the silicon wafer. Subsequently, a metallic film was sputtered onto the silicon dioxide. The silicon dioxide was grown onto the silicon wafer to prevent current from

conducting away from the deposited metal layer via silicon and the stainless steel clamp. At the same time, the silicon dioxide layer was used to prevent any diffusion of metal atoms into the bulk silicon substrate. The metallic layer was sputtered onto the silicon dioxide such that both the base substrate and the workpiece acted as electrodes when the electric potential was supplied to them. The deposited metal layer had to be reasonably thick enough (500 nm) to ensure that no electrical breakdown of the electrode occurred due to the high potential difference during the experimental study. An outline of the equipments used during the fabrication of the fluidic channel is documented in Appendix A.

Fig 3.3 Transparency mask

Channel dimensions were designed by using a commercial software (L-edit[®]) and a transparency mask as shown in Fig 3.3 was produced. The transparency mask was generated such that the photolithography process could be performed to form a channel on the base substrate. Though-hole reservoirs at the end of each channel were formed using deep reactive ion etching (DRIE, STS) to provide an inlet and exit for fluid flow in

the channel. Nanoport adapters (Churchill assemblies), aligned to the hole reservoirs, were then attached to the base substrate. A clamp was designed to provide a tight seal between the wafer and workpiece to minimize fluid from leaking out of the channel when the liquid was being pumped through.

Fig 3.4 Fluid pumping device

The slurry, which consisted of colloidal particles in the fluid, was pumped into the channel via the Nanoport assemblies with the aid of a pumping device as shown in Fig 3.4. At the same time, an electrical voltage was supplied to the electrodes via voltage probes and wires that were soldered onto them. The electrical voltage was supplied onto the test structure with the use of a function generator (Tektronix AFG 3022) and a DC voltage amplifier (Cambridge Piezo Systems, MA, EPA-102). An oscilloscope was subsequently engaged to monitor the voltage potential between the electrodes.

For the set of experiments to study the dynamic behaviour of the colloidal particles, an indium tin oxide (ITO) glass was used for the top substrate (acting as the workpiece) as it is transparent. A colloidal solution of fluorescent polystyrene particles was pumped into the channel and an inverted microscope with an attached CCD camera was used for visualization.

For the set of experiments to study on the material removal, a colloidal solution of abrasive particles was pumped into the channel over a span of typically 1 hour for material removal to take place. The workpiece was subsequently characterized to study the material removal on the surface and to identify the more likely material removal mechanism that took place during the experiment.

The setup for both set of experiments is shown in Fig 3.5.

Fig 3.5 Experimental setup

3.1.2 Experimental procedures

To look at the feasibility of using electric field activated abrasive particles to achieve material removal on a workpiece, a base substrate consisting of a channel for fluid flow was fabricated. The channel was constructed to study the fundamental aspects of the motion of the abrasive particles within the flow of the slurry under the influences of several parameters (such as applied voltage, frequency and fluid velocity). Experiments were subsequently undertaken to study the removal on the workpieces under these influences.

Since the leakage of the fluid along the fluidic channel, fluid types, abrasive particle types and the material of the workpiece might affect the study of the electrokinetic material removal, preliminary studies on these areas were made.

The study of the material removal of the workpiece was only made when the design of the fluidic channel for the base substrate, selection of dielectric fluid, abrasive particles and workpiece material were decided. Experiments were then prepared to study the parametric effects on the material removal of the workpieces during the electrokinetic material removal process. The experiments were undertaken to study the removal on the workpiece over a span of time of typically 1 hour.

Appropriate characterization techniques were employed to determine the material removal depth and the surface roughness of the channels on the workpiece after the material removal process. The material removal rate was calculated by dividing the material removal depth over the span of time of the material removal process. For each data point on each graph that are presented in the subsequent chapter, a total of 10 measurements (across the channel) were made. Outliers from each set of measurements were removed such that a more robust and accurate account on the material removal for each data point would be reflected. The sample mean and standard deviation of the material removal for each data point was then calculated and plotted on each graph.

3.2 Characterization techniques

Characterization techniques are measurement methods that are used to observe, measure or quantify certain parameters on the subject of interest in a quantitative or qualitative manner. The quantitative results are used to compare the parameters on the subject of interest with a standard measurement while the qualitative results are obtained to observe the subject of interest in a pictorial manner.

In this section, only selected characterization techniques that are used during the experimental studies were included. As such, common characterization techniques (e.g.

scanning electron microscopy (SEM) and tunnelling electron microscopy (TEM)) that were used during the experimental studies, will not be included in this section. Some of the characterization methods that were used to obtain the quantitative results were the zeta potential analyzer, the white light interferometer, the mechanical stylus profiler, the atomic force microscopy (AFM) and the X-ray photoelectron spectroscopy (XPS) while the qualitative results (for the observation of the trajectory of the particles) were obtained from the inverted optical microscope.

3.2.1 Zeta potential analyzer

To characterize the colloidal abrasive particles, a zeta potential analyzer was used. The zeta potential analyzer (Malvern Instrument Zetasizer Nano ZS) determines the size and the zeta potential of the particles by utilizing the light scattering technique in the instrument. The instrument is capable of measuring particles in the range of 0.6 nm to 6 μm range and does not require much dilution during the measurement. Coincidentally, the sizes of the particles that were considered in the experiment setup fell within this range. On top of that, comparisons of the various colloidal particles are made possible as the concentration of the particles within the slurry affects the zeta potential of the particles [92]. The distribution of size and zeta potential for one of the particles that was obtained from the instrument is as shown in Fig 3.6.

Fig 3.6 Distribution of size and zeta potential for colloidal polystyrene particles in deionised water

3.2.2 White light interferometer

The white light interferometer (WYKO NT3300 from Veeco) was used to determine the material removal of the workpiece. It is a non-destructive technique for measuring the features of interest. The WYKO instrument was operated in the vertical scanning interferometry (VSI) mode which provided a vertical range of 500 μm with a resolution of 3 nm.

In the experiment, the depths of the material removal were characterized by the white light interferometer especially when it is able to give the attraction of providing a 3D geometrical measurement of the features.

Fig 3.7 White light interferometer (WYKO NT3300)

3.2.3 Mechanical stylus profiler

A mechanical stylus profiler (Dektak³ST from KLA-Tencor) was used to determine the material removal of the workpiece. The Dektak profiler was used to measure the surface roughness and the material removal step on the workpiece. It has the capability of vertical range from 10 nm to 131 μm with a vertical resolution of 1 $\text{\AA}$ /6.5 μm , 10 $\text{\AA}$ /65.5 μm and 20 $\text{\AA}$ /131 μm respectively. The machine can perform scan length range from 50 μm to 50mm at scan speed ranges of low, medium and high. The scan time range of the profiler is between 3 to 50 seconds. However, the drawback of the mechanical stylus profiler is that it can only execute single line scan.

In the experiment, measurements from the mechanical stylus profiler were used to confirm with those from the white light interferometer.

Fig 3.8 Dektak surface profiler

3.2.4 Atomic force microscopy (AFM)

Atomic force microscopy (S3000 from Digital Instrument) is a mechanical scanning probe microscopy that is able to detect very precise features at extremely high resolution. It has the capability to scan features in the atomic resolution. In fact, the AFM has always been one of the preferred characterization equipments when it comes to measuring surface roughness at the nanometric level [130-132].

The AFM was used to characterize the surface roughness of the workpiece after undergoing the electrokinetic material removal process. During the measurement, the tapping mode was used. The tapping mode was used as it is able to minimize the lateral forces and reduce damages on the surface of the workpiece during scanning. Therefore, possible problems during the measurement such as frictional effects and adhesion issues are minimized. The AFM that was utilized for the measurement is shown in Fig 3.9.

Fig 3.9 Atomic force microscopy (S3000 from Digital Instrument)

3.2.5 X-ray photoelectron spectroscopy (XPS)

The XPS was utilized during characterization to study the elemental composition, empirical formula, chemical state and electronic state of the elements that exist in the surface of the specimen. Moreover, XPS is much more sensitive than EDS where it is able to detect the elements in the specimen down to 1000 parts per million (ppm) level as compared to the latter. As compared to the EDS, the depth of penetration during the XPS characterization is much lower too (~ 10 nm).

3.2.6 Inverted optical microscope

The inverted optical microscope (Leica DMILM) was used to observe liquid leakage when the particle suspended fluid was pumped into the fluidic channel. The optical microscope was also used to observe the particle trajectories when the electrical voltage

was supplied to the test structure. The microscope is equipped with a filtered mercury lamp source that allows fluorescent polystyrene particles to be visualized more clearly.

Fig 3.10 Inverted optical microscope (Leica DMILM)

3.3 Summary

In this chapter, the experimental setup and procedures of the electrokinetic material removal technique were presented. In addition, the characterization techniques to measure and inspect the material removal on the workpiece were also mentioned. The results of the experiments that were conducted during the study of the research will be covered in the following chapter.

Chapter 4

Results and discussion on material removal due to electrokinetic phenomenon

In this chapter, results on the selection of the fabrication methods and material selection for the experimental study will be presented and discussed. An overview of the chapter is shown in Fig 4.1.

With reference to Fig 4.1, this chapter will be divided into four sections. Section 4.1 will present the electrokinetic material removal technique and discuss the preliminary results on the feasibility of the electrokinetic material removal process. Section 4.2 will then present the influences of the electrokinetic and the hydrodynamic effects on the electrokinetic material removal process and discuss the relationship between these parameters and the material removal rate on the workpiece. Following that, section 4.3 will present the particle effect dependency on the material removal process. Subsequently, a chapter summary will be included.

Fig 4.1 Overview of Chapter 4

4.1 Preliminary results and discussion on the feasibility of the electrokinetic material removal process

4.1.1 Electrokinetic material removal technique

To achieve material removal using electrokinetic phenomenon, a combination of the AC and DC electric field should be applied to the test structure; where an AC electric field is required to oscillate the colloidal particles and a DC electric field is employed to bring the particles nearer to the workpiece. In order to ensure constant, uniform material removal from a surface, there should be a need to add a horizontal component of particle motion exerted by flowing fluid.

Fig 4.2 The trajectories of the particles when they are under the influences of fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only (d) AC electric field with a DC bias.

An illustration of the particles' idealized motion is shown in Fig 4.2 with the fluid flowing from the left to the right between the two parallel electric field plates (electrodes). Fig 4.2 (a) demonstrates the horizontal motion of the particle in the x-

direction due to the hydrodynamic effect only while Fig 4.2 (b)–(d) show the motion of the particle when it is under the influences of both the hydrodynamic and different electrokinetic effects. When the particle is under the influence of an alternating current (AC) electric field only (Fig 4.2 (b)), the particle is expected to make oscillations across the centre of the channel due to the electrical polarity switching with a strong possibility of only a relatively few interactions occurring between the particle and the workpiece. When the particle is merely under the influence of direct current (DC) electric field (Fig 4.2(c)), the particle is brought to closer proximity with the surface of the workpiece to enhance particle interactions with it. It is only with the combination of the AC and DC electric fields (Fig 4.2(d)) that cyclic collisions of the particle with the surface of the workpiece are expected to result in material removal. From the diagrams in Fig 4.2, dielectrophoresis and electrorotation should be considered negligible as there are no electric gradients between the electrodes.

Once the suggested electrokinetic effect was selected, material removal experiments based on the proposed effect was carried out for the research study. During the experiments, it was ensured that a fresh supply of abrasive particles was continuously delivered during the material removal process.

Since the leakage of the fluid along the channel, fluid types, abrasive particle types and the material of the workpiece might affect the study of the electrokinetic material removal, prior studies on these areas were made.

4.1.2 Fabrication methods of fluidic channel

During the fabrication of the fluidic channels, a setup that allowed easy removal of the base substrate from the workpiece was desired. Consequently, a design that could fulfil these requirements was selected.

Several base substrate designs were considered and they were tested by using a microscope to view at the leakage of the fluid along the channel. The comparison of these base substrate designs are shown in Table 4.1.

Table 4.1 Different approaches to fabricate the fluidic channels

No.	Designs for the base substrate	Fabrication methods for the base substrate	Comments
1		<ol style="list-style-type: none"> 1. Photolithography was carried out to pattern the channel structures on the silicon wafer before deep reactive ion etching (DRIE) was performed to achieve the fluidic channel 2. Oxidation was carried out to form a layer of silicon oxide on the surface of the wafer before gold was deposited onto the channel region 3. Photolithography by using backside alignment was employed to pattern the holes for the inlet and the outlet of the channel before DRIE was further performed to produce through holes for the fluid to flow into and out of the channel 	<ul style="list-style-type: none"> • Gold seemed to deposit onto the walls of the silicon channel during sputtering • Considerable fluid leakage was observed
2		<ol style="list-style-type: none"> 1. Oxidation was carried out to form a layer of silicon oxide on the surface of the channel before gold was deposited onto the silicon oxide layer 2. Photolithography was performed to form a photoresist (SU8) fluidic channel on top of gold 3. Photolithography by using backside alignment was employed to pattern the holes for the inlet and the outlet of the channel before DRIE was further performed to produce through holes for the fluid to flow into and out of the channel 	<ul style="list-style-type: none"> • Considerable leakage was observed
3		<ol style="list-style-type: none"> 1. Oxidation was carried out to form a layer of silicon oxide on the surface of the channel before gold was deposited onto the silicon oxide layer 2. Photolithography was performed on top of gold to form channel structures (SU8) 3. Photolithography by using backside alignment was subsequently employed to pattern the holes for the inlet and the outlet of the channel before DRIE was further performed to produce through holes for the fluid to flow into and out of the channel 4. Siloxane (PDMS) was then poured on top of gold and allowed to cure 5. Reactive ion etching was employed to remove the cured PDMS on top of the photoresist before the photoresist was consequently removed to form PDMS channel 	<ul style="list-style-type: none"> • Leakage seemed to be lesser than the other two methods

Out of these designs, method 3 appeared to be the best. The design of the substrate allowed easy separation of the workpiece so that the surface material removal could be characterized. On top of that, design 3 was ultimately chosen due to its sealing ability which resulted in minimum leakage as compared to the other two fabrication designs as shown in Fig 4.3.

Fig. 4.3 Comparisons of the fluidic leakage due to base substrate (a) design 1 and 2 (b) design 3

Leakage from the PDMS (polydimethylsiloxane) channels was also further minimized by clamping the base substrate and the workpiece together. A diagram of the base substrate with the PDMS channel is shown in Fig 4.4.

Fig. 4.4 A diagram of base substrate with the PDMS fluidic channel

As mentioned earlier in the previous chapter, the silicon oxide ($1\ \mu\text{m}$) was grown onto the silicon wafer to prevent electricity from conducting away from the deposited metal layer via silicon. Also, the deposited metal layer had to be reasonably thick enough ($500\ \text{nm}$) to ensure that no electrical breakdown of the electrode occurred due to the high potential difference during the electrokinetic process. The channel in the PDMS was $500\ \mu\text{m}$ wide and $25\ \mu\text{m}$ deep ($20\ \mu\text{m}$ after compression during clamping) and was fabricated by the process [133] described in Fig 4.5

Fig. 4.5 A schematic diagram of the overall fabrication process of the base substrate. (a) Silicon wafer was oxidized to form a layer of silicon dioxide (b) A layer of metal was deposited on top of the silicon dioxide layer (c) Photoresist was patterned on top of the gold layer to form channel structures (d) Backside alignment and exposure of resist was done such that deep reactive ion etching process could be executed to produce through-holes for the fluid to flow into the channel (e) PDMS (Dow Corning Sylgard 184) was applied onto the wafer. After curing, reactive ion etching was employed to remove the PDMS material on top of the photoresist [134] (f) Photoresist was removed to form a PDMS channel.

Once the channel on the base substrate was fabricated, the experiments on the material selections were carried out in the search for the most appropriate material for the electrokinetic material removal study.

4.1.3 Selection of fluid

During the experimental studies, only dielectric fluid was considered. The fluid was selected to eliminate or minimize the possibility of material removal due to electrochemical methods. Subsequently, dielectric fluid was selected on the basis of their dielectric strengths. During the selection, the fluid was pumped into the test structure at a

standardized flow rate (fluid velocity: 0.1 m/s) and the voltage supply between the electrodes was tuned until a breakdown of the fluid was observed. A DC electric field was applied to the electrodes with the workpiece being positive biased and the base substrate negative to record the electrical breakdown strength of the dielectric fluid. The fluid that possessed the highest electric breakdown strength was selected for future material removal experiment.

Fluid selection was restricted by two criteria; the fluid must be a dielectric medium and preferably environmentally benign. Suitable candidates were narrowed down to deionised water, organic solvents and EDM fluid (Daphne HL25 supplied by Idemitsu). Deionised water was rejected due to the lower dielectric strength (as compared to the other two). Due to concerns about the level of hydrocarbon content in the EDM dielectric fluid which could pose a degradation problem to the rubber seals of the syringe, organic-based solvents were selected. Three solvents; ethanol, propan-2-ol and propan-2-one, were short-listed with the latter then being rejected due to its level of toxicity.

Table 4.2 shows a comparison between ethanol and propan-2-ol on their respective dielectric strengths. Ethanol was ultimately chosen although it had slightly lower dielectric strength. Propan-2-ol, when inhaled, is oxidized by the liver system into acetone which can cause symptoms such as headaches, nausea and vomiting.

Table 4.2 Dielectric strengths of various dielectric fluids

Dielectric fluid	Dielectric strength (kV/cm)
Ethanol	125
Propan-2-ol	135
Deionised water	50
EDM Fluid	400

4.1.4 Selection of abrasive particles

Colloidal particles were selected on the basis of the zeta potential and the size of the available particles. The particles that exhibited the highest zeta potential were selected. The size of the particles were also taken into consideration as particles that were too

small ($< 1 \mu\text{m}$) may be subjected to the more dominant Brownian motion while particles that were too large ($> 10 \mu\text{m}$) were subjected to sedimentation due to gravitational pull. Thus, particles in the range of $1\sim 10 \mu\text{m}$ were considered as the best candidates to avoid these issues [135-139].

Selection of the abrasive particles suspended in the dielectric fluid was undertaken. Average particle size and distribution were determined using the zeta potential analyzer and the particle shape was observed through transmission electron microscopy.

A number of abrasive particle types were considered which included aluminium oxide, silicon carbide, diamond and silicon oxide. The zeta potential analysis was carried out with the various types of particles suspended in ethanol. Table 4.3 shows the zeta potential values of these particles. For these experiments, particles exhibiting larger magnitude of zeta potential are desirable as they carry a larger surface charge which result in greater impact onto the surface of the workpiece during each cycle of collision, according to equation (2.7).

Table 4.3 Zeta potential values for the various types of abrasive particles

Abrasive particles	Zeta potential (mV)
Aluminium oxide ($1.0 \sim 1.5 \mu\text{m}$)	-56.5
Diamond ($3.0 \mu\text{m}$)	-36.4
Silicon carbide ($6.0 \mu\text{m}$)	-19.1
Silicon oxide ($1.5 \mu\text{m}$)	-64.5

Silicon oxide which has the highest magnitude in zeta potential was selected. Silicon (IV) oxide particles of 1.5 microns in diameter (supplied by Alfa Aesar) were used. The particle morphology was analyzed using the TEM as shown in Fig 4.6 and was determined to be spherical in shape.

Fig. 4.6 TEM image of silicon (IV) oxide particles

Ethanol containing the selected suspended abrasive particles was subsequently introduced into the channel using a syringe pump and the fluid dielectric strength experiment as mentioned in section 4.1.3 was performed.

The dielectric strength of the slurry (silicon oxide particles suspended in ethanol) was measured and was recorded to be approximately similar to the dielectric strength of pure ethanol in Table 4.2. The result supported that reported by Wong *et al* [140] in that the inclusion of particles into the dielectric fluid had only a minor influence on the electrical strength of the dielectric fluid.

4.1.5 Selection of material for the workpiece

Selection of the appropriate material for the removal process was important to accurately determine the material removal mechanism. Since the main area of interest in this study is to understand the mechanical material removal mechanism, other possible non-mechanical mechanisms, that might be evident in the material removal, have to be eliminated.

Material for the workpiece had to be carefully considered. The main requirements for the material were that it should be chemically inert as well as able to be easily deposited onto the substrate. Inertness was considered to be critical as the formation of oxides on the surface could substantially influence the removal process. This is because if an inappropriate material is used during the experiment, it becomes very difficult to account for the material removal of the workpiece. Thus, materials that do not oxidize readily to liquid were considered as the best candidate for the electrode and workpiece.

Ultimately, gold material was selected for most of the studies. Both electrodes (the base substrate and the workpiece) were coated with gold material in order to eliminate factors such as electrochemical corrosion which could amount to an inaccurate material removal rate for the mechanical aspect of the material removal process. During the experimentation, it was ensured that the metallic surface was not entirely removed such that the material material removal rate could be determined more accurately where material delamination issues would be easily identified.

4.1.6 Preliminary material removal results

Preliminary results appeared to be promising as initial results showed that the electrokinetic phenomenon appeared to be capable of achieving nanometric material removal. This is demonstrated by the results as shown in Fig 4.7 and 4.8.

Fig 4.7 White light interferometer (WYKO) top view image of the material removed from a gold workpiece with a 2-D profile on the material removed from the gold workpiece in the X direction (direction perpendicular to the channel situated at the centre of the channel) and a 2-D profile on the material removed from the gold workpiece in the Y direction (direction along the channel situated at the centre of the channel)

Fig 4.8 SEM picture with white arrows pointing to the channel walls

During the material removal, it was observed that there might be greater material removal at the edges of the channel. One possible explanation could be due to the localized non-homogeneities of the electric field where the electric field lines are more concentrated at the edges as PDMS has a higher electrical resistivity ($4 \times 10^{13} \Omega \text{ m}$) as compared to ethanol ($1.8 \times 10^8 \Omega \text{ m}$) [141]. This difference could have caused greater material removal near the channel edges as compared to the channel centre.

Other than looking at the capability of achieving nanometric material removal on the workpiece, efforts were also made to look into the uniformity of the material removal along the direction of the channel (Y direction) as shown in Fig 4.9.

Fig 4.9 shows the uniformity of the material removal along the channel of the workpiece. It was evident that the material removed along the channel was relatively uniform over a length of $1200 \mu\text{m}$. Similar profiles along the channel after the material removal process were also obtained. It was observed that the material removal obtained from Fig 4.9 was approximately 100 nm throughout the entire channel. This rendered the process utilizing the electrokinetic phenomenon capable of producing relatively uniform material removal along the channel.

Fig 4.9 Uniformity of material removed along the channel on the workpiece

Besides the material removal rate and the uniformity of the material that was removed from the surface of the workpiece, a preliminary study on the surface roughness of the workpiece after the material removal process was also made. A comparison was carried out between the surface roughness of the workpiece before and after the material removal process as shown in Fig 4.10.

Fig 4.10 Surface topography of the gold workpiece before and after the material removal process

It was observed that the surface roughness of the workpiece after the material removal process was approximately in the range of 2 to 20 nm RMS as the value depends on the set of parameters that were carried during the process. This makes the process a very attractive material removal one as it serves as an alternative method to provide polishing at the nanometric orders as compared to the current options such as the EEM [142] or ultraprecision diamond cutting systems [143]. For a better understanding on the surface finish that the electrokinetic material removal process can produce, a more detailed surface roughness analysis will be presented in Chapter 7.

To visualize the dynamic behaviour of the particles within the channels, the workpieces were replaced by an ITO coverslip. Fluorescent latex polystyrene particles (Duke Scientific) of $1.5\ \mu\text{m}$ (suspended in deionized water) were introduced into the channel. Coincidentally, the zeta potential of the polystyrene beads are approximately $-55\ \text{mV}$ and are rather close to the value obtained from the silicon oxide abrasive particles. When an AC electric field was applied to the test structure at a low flow rate, particle “blinking” was observed through the microscope as shown in Fig 4.11.

Particle “blinking” suggested that the fluorescent beads were going into and out-of-focus as the AC cyclic waveform moved from positive to negative. This would imply that the particles were moving closer to and then further away from the ITO coverslip as the waveform cycled. At low frequencies the trend was clearly apparent. However, for higher frequencies, the trend was not so clear as the particles were moving faster which made visualization more difficult.

(a)

(b)

Fig 4.11 The sequence in the motion of the particle when viewed through the ITO coverslip under the influences of (a) hydrodynamic effect only (b) both hydrodynamic and electrokinetic effects

To further examine the behaviour of the particle, an experimental setup was performed such that the impingement of the particles onto the surface of the workpiece could be visualized clearly in the cross sectional view to validate the hypothesis on the ideal motion of the particles. The recorded sequence of the particle is shown in Fig 4.12.

It was also observed that the position of the particles could be controlled further by introducing a DC bias. A positive bias resulted in particles moving closer to the coverslip where a negative bias forced particles down to the base substrate. It was observed that higher voltages resulted in more dramatic particle movement while lower voltages caused less noticeable to no apparent movement. The observations were expected and were in good agreement with the trajectories of the particles as illustrated previously in Fig 4.2.

(a)

(b)

Fig 4.12 The sequences in the motion of the particle when viewed in the cross sectional view under the influences of (a) hydrodynamic effect only (b) both hydrodynamic and electrokinetic effects (with the arrows tracing the motion of the particle)

During characterization of the material removal from the workpiece, the observations obtained suggested that the primary material removal mechanism was that of a mechanical one (erosion material removal process). Other material removal mechanisms were regarded as insignificant as there was insufficient evidence to suggest their presence and influence. Some of the possible material removal mechanisms that could be present in the material removal include electrical discharge machining (EDM) and galvanic corrosion. However, EDM could not be identified as the process that is responsible for the material removal of the workpiece as there was insufficient presence of craters to suggest so. Galvanic corrosion could not be the main mechanism also as the fluid that was utilized during the process was a dielectric one. This consequently led us to suggest that the mechanical material removal mechanism to be the most possible method as the net resultant velocity of the particles exceeds the energy required to break the metallic bond of the atoms in the workpiece.

During the material removal process, it was observed that the material removal was related to the process time. Fig 4.13 shows the relationship of the material removal over a duration of 75 minutes of process time. The material removal appeared to be progressive during the removal process with an increment of approximately 600 Angstroms in every 15 minutes. This gave a material removal rate of approximately 2400 Angstrom/Hr.

Fig 4.13 Material removal of gold over process time (Silicon oxide particle size: $1.5\mu\text{m}$, particle concentration: 0.01g/ml , fluid velocity: 0.4 m/s , DC electric field strength: 12.5 kV/cm , AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

4.2 Results and discussion on the influences of electrokinetic and hydrodynamic effects on the material removal process

Once the evidence of material removal by electrokinetic phenomenon was shown, further experiments were carried out to determine the relationship between the rate of material removal and electrokinetic/hydrodynamic effects. Subsequently, an experimental table as shown in Table 4.4 was designed to study the relationship between the influencing parameters and the material removal rate of the gold workpiece (gold sputtered wafer where the purity of the sputter target for the sputtering process is 99.99% pure gold (Super Conductor Materials, Inc)). Through understanding these parameters only then will it be possible to manipulate and control the dynamic behaviour of the abrasive particles and hence the removal rate.

Experiments were undertaken to study the removal rate on the gold workpiece under the influences of different possible parameters such as:

- DC electric field strength
- AC electric field strength
- AC electric field frequency
- Fluid velocity

For the following results, the WYKO white light interferometer and the Dektak surface profiler were used to determine the material removal depth of the channels on the workpieces. The material removal rate was calculated by dividing the material removal depth over the span of time of the material removal process. The process time was set at 1 hour for the experiments as the trenches (channels) formed on the workpiece after the material removal process would be deep enough for accurate characterization. For process repeatability issues, it should be noted that the runs for each data point were repeated at least twice. Subsequently, for the data points on each graph that are presented in the subsequent experiments, a total of 10 measurements (across the channel) were made. Outliers from each set of measurements were removed such that a more robust and accurate account on the material removal rate for each data point would be reflected. The sample mean and standard deviation of the material removal depth for each data point was then calculated and plotted on each graph.

Table 4.4 Experiments carried out to study the influences of electrokinetic and hydrodynamic parameters on the material removal rate

Experiment	Time	Particle type	Particle size	Concentration of particles	DC electric field strength	AC electric field strength (pk-pk)	AC electric field frequency	Fluid velocity
	(min)							
Experiment 1 (Fig 4.14)	60	Silicon oxide	1.5	0.01	0~30.0	50	10	0.40
Experiment 2 (Fig 4.15)	60	Silicon oxide	1.5	0.01	12.5	20 ~100	10	0.40
Experiment 3 (Fig 4.16)	60	Silicon oxide	1.5	0.01	12.5	50	0 ~ 500	0.40
Experiment 4 (Fig 4.17)	60	Silicon oxide	1.5	0.01	12.5	50	10	0.05 ~ 1.40
Experiment 5 (Fig 4.18)	60	Silicon oxide	1.5	0.01	12.5	30 ~100	10	0.2 ~ 0.6

4.2.1 Influence of DC electric field strength on the material removal rate of the workpiece

Fig 4.14 The influence of DC electric field strength on the material removal rate of gold workpiece

Fig 4.14 shows the relationship between the DC electric field strength and the material removal rate of the process. It was observed that the material removal rate increased from 0 kV/cm to 12.5 kV/cm before it started to decrease.

When there was no DC electric field, the particles were mainly oscillating about the centre of the channel with very few collisions between the particles and the surface of the workpiece. It was only with the introduction of the DC electric field that the probability of interactions between the particles and the surface of the workpiece increased. In addition to more particle collisions with the surface of the workpiece, the application of the DC electric field also provided higher velocity and larger angle of impingement for the particles. Hence, a rise in the material removal rate was observed with increasing DC electric field strength.

However, when the DC electric field strength was increased further, the material removal rate started to decrease. This is because when the DC electric field strength was too high, the particles were not able to oscillate with sufficient amplitude to gain enough velocity

to cause maximum material removal. When the DC electric field strength exceeded 25 kV/cm, the particles were not able to oscillate as the DC electric field strength had exceeded the amplitude of the AC electric field where the peak-to-peak (pk-pk) AC electric field strength was 50 kV/cm. Hence, DC electric field strengths beyond 25 kV/cm were not investigated for the rest of the report. It was assumed that the material removal mechanism had differed from the intended mechanism as it had shifted from the impingement to mainly frictional material removal mechanism. The material removal rate, when DC electric field strength was 25 kV/cm and beyond, was observed to be approximately 400 Angstrom/Hr.

4.2.2 Influence of AC electric field strength on the material removal rate of the workpiece

Fig 4.15 The influence of AC electric field strength (pk-pk) on the material removal rate of gold workpiece

Fig. 4.15. shows the relationship between AC electric field strength and workpiece removal rate. It is observed that there is a rise in the material removal rate when the AC electric field strength increased from 20 kV/cm to 50 kV/cm. With a higher AC electric field strength, a higher material removal rate was achieved due to increasing velocity at larger angle of impingement on the workpiece. Fagan *et al* [102] conducted a similar experimental setup to study the vertical oscillatory motion of a single colloidal particle

along the AC electric field across the electrode. They reported that the motion of the particle was related to the electric field strength where the amplitude of the oscillatory motion of the particles in the applied field increased with higher amplitude of the AC electric field.

At the same time, the interaction of the particles with the surface of the workpiece was expected to rise due to the higher AC electric field strength (refer to section 5.2.1). This is because the higher AC electric field strength promoted the participation of the particles during each cyclic collision for higher material removal [111].

The trajectory of the particles changed as the horizontal component (fluid flow) became less dominant with increasing electric field strength. The angle of particle impingement towards the surface may have reached an optimum for material removal where it was believed that the material removal mechanism might have shifted from friction (small angle of impingement due to the sliding of the particles onto the surface of the workpiece) to impingement (larger angle of impingement where the workpiece is abraded away due to the collision of the particles).

However, the material removal rate began to decrease with further increase in electric field strength. During the increase in AC electric field strength, the trajectories of the abrasive particles were altered when the horizontal component (fluid flow) became less dominating as compared to the higher electric field strength which resulted in the declining removal rate trend after the optimum material removal rate was achieved.

During the study, it was observed that the behaviour in the material removal followed the same trend observed by Finnie *et al* when investigating free abrasive erosion [104,112]. In his work, Finnie observed that the material removal was at its maximum at a particular angle of impingement for various materials. He observed that the angle for maximum material removal rate occurred at approximately 20° for the gold [117]. In our work, it is believed (and later shown in section 5.2) that the angle of impingement at the maximum material removal rate coincided with the value that was reported by Finnie.

It was also observed that the material removal rate was approximately 400 Angstrom/Hr when the AC electric field strength (pk-pk) was approximately 25 kV/cm. This, in comparison with the point where the AC electric field amplitude and the DC electric field strength were of the same magnitude as shown in Fig 4.14, brought us to the same material removal rate as the particles were dragged along the surface of the workpiece with the same fluid velocity and same mode of material removal mechanism (friction).

4.2.3 Influence of the frequency of AC electric field on the material removal rate of the workpiece

It was observed that the material removal rate rose as the AC electric field frequency increased from 0 Hz to 10 Hz. The rise in the material removal rate was due to the increase in the participation of the abrasive particles during the material removal process. However, when the AC electric field frequency was increased beyond an optimal of 10 Hz, the material removal rate started to decrease as shown in Fig 4.16. The trend was obvious where the material removal rate declined with increasing AC electric field frequency beyond 10 Hz although more particles would be expected to approach the surface of the workpiece within a fixed amount of time at a higher frequency. This is because, when the frequency of the electric field was too high, the particles were unable to respond to the electrostatic force fast enough to collide onto the surface for material removal before being pulled in the opposite direction during each cycle. Similar observations were made by Fagan *et al* [102] where they reported that the height levitation of the particles decreased with increasing AC frequency in their setup that is similar to the one reported here. It was reported that the particle was not able to move as great a distance towards the surface as it can move away from the surface for the same applied force at high frequencies during each cycle. Conversely, at lower frequencies, the particle had time to travel further during each cycle, which increased the amplitude of the oscillation, giving the particle the opportunity to oscillate more. This can be conceived by increasing the frequency value in equation (2.7) where the velocity of the particle due to the vertical electrostatic effect is reduced. During the experimental study, material

removal rate remained at a constant low range of around 400 Angstrom/Hr beyond a frequency of around 400 Hz which further supported the above observations.

Fig 4.16 The influence of the frequency of AC electric field on the material removal rate of gold workpiece

4.2.4 Influence of the fluid velocity of the dielectric fluid on the material removal rate of the workpiece

Fig 4.17 The influence of the fluid velocity of the dielectric fluid on the material removal rate of gold workpiece

Fluid velocity of the dielectric fluid is another factor that could affect the material removal rate of the workpiece. Flow rate (which is related to fluid velocity) of the dielectric fluid can have a noticeable influence on the material removal rate of the workpiece as it provides the hydrodynamic effect on the particles by varying the fluid velocity that they entrain. A trend was observed when the fluid velocity of the dielectric fluid was varied from 0.05 to 1.4m/s as shown in Fig. 4.17. The removal rate of the material reached a maximum of 2500Angstrom/Hr at 0.4m/s before decreasing to around 1100 Angstrom/Hr at 1.4m/s. This can be explained in a similar way to that for the electric field which provides the vertical component of the particle motion. The angle of impingement to the surface may have reached a critical value at around 0.4m/s before the material removal rate started to decrease. An explanation for the increase in material removal rate was due to the faster approach of the particles onto the surface of the workpiece at higher fluid velocities to cause more material removal. However, this showed otherwise as the fluid velocity passed beyond the 0.4 m/s mark. The decrease in the material removal rate of the gold workpiece beyond fluid velocity of 0.4m/s could be that the fluid velocity was too high such that the particles did not have the opportunity to collide/interact with the surface. Although the impact velocity of the abrasive particles played a substantial role in the material removal process, the angle of impingement and the participation of the abrasive particles, coupled with the particles' interaction with the workpiece surface seemed to be even more crucial as the material removal rate decreased after 0.4 m/s with increasing fluid velocity which is shown in Fig. 4.17. Although higher particle velocity might infer greater material removal on the workpiece, the angle of impingement and the participation of the abrasive particles, coupled with the particles' interaction with the workpiece surface, were too low for considerably high material removal to occur.

Conversely, although the angle of impingement and the participation of the abrasive particles, coupled with the particles' interaction with the workpiece surface, largely affect the removal rate of the material, a decrease in the material removal rate from fluid velocity of 0.4 to 0.05 m/s was observed. This is because, when the velocity is too low, insufficient energy was available to remove the material away from the workpiece.

4.2.5 Influence of AC electric field strength on the material removal rate of the workpiece with different fluid velocities

Fig 4.18 The influence of AC electric field strength (pk-pk) on the material removal rate of gold workpiece at different fluid velocities

To further study the relationship between the AC electric field strength and the fluid velocity on the material removal rate, additional experimentation was undertaken. It was observed in Fig 4.18 that the maximum material removal rate occurred at different AC electric field strength for different fluid velocities. The optimal material removal rate for the abrasive particles took place at approximately 40 kV/cm, 50 kV/cm and 70 kV/cm for fluid velocity of 0.2 m/s, 0.4m/s and 0.6 m/s respectively. The results corresponded to an angle of impingement of approximately 20° for the optimal material removal for each of the fluid velocities of 0.2 m/s, 0.4m/s and 0.6 m/s respectively. The results agreed with the conclusions that were made by Finnie in his previous work [117].

4.2.6 Design of experiment study on electrokinetic and hydrodynamic effects on material removal rate

Since DC electric field strength, AC electric field strength, AC electric field frequency and fluid velocity were reported to affect the trajectory of the abrasive particles, which in turn influence the material removal rate of the process on the gold workpiece, a design of experiment (DOE) was carried out. The DOE was undertaken to determine the dominating parameter effect amongst these factors.

During the DOE study, a 3 level full factorial design was utilized. Table 4.5 tabulates the factor assignment of the 4 factors.

Table 4.5 Assignment of factors for DOE study

Factors	Assignment	Number of levels (L)	L₁	L₂	L₃
DC electric field strength	(A)	3	0.0 kV/cm	12.5 kV/cm	25.0 kV/cm
AC electric field strength (pk-pk)	(B)	3	30.0 kV/cm	50.0 kV/cm	100.0 kV/cm
AC electric field frequency	(C)	3	7.5 Hz	10.0 Hz	500.0 Hz
Fluid velocity	(D)	3	0.2 m/s	0.4 m/s	1.4 m/s

For the DOE study, a total of 81 single replicate runs were performed. The DOE was undertaken to investigate the main effects of the factors and their interactions. A statistical software (Minitab 15) was utilized to carry out the DOE study. An analysis of variance (ANOVA) was generated based on the response of the 81 single replicate runs. The ANOVA for the DOE study is documented in Appendix B

The ANOVA was initially carried out on the assumption that interactions effects were less significant. This was proven to be the case from the results taken from the ANOVA. Therefore, during the analysis for the DOE, high order interactions (which involve 3 factors and 4 factors interactions) were assumed to be negligible where the interaction

mean squares were used as error mean squares (MS_E) to test for the hypotheses of the main effects.

Fig 4.19 Main effects plot for material removal rate

Fig 4.20 Interaction plot for material removal rate

According to the results from the ANOVA, it was realized that the main effects of the 4 factors were significant at a confidence level of 5%, with the factors of DC electric field strength and AC electric field frequency as the most significant. Amongst the interaction effects, only effects of AB and AC are significant at 5% confidence level. The graphs for the main effect plots of the 4 factors are shown in Fig 4.19 while the interaction plots are shown in Fig 4.20.

Between the main effects, DC electric field strength was statistically determined to be the most significant. This may be attributed to the increase in the participation of the abrasive particles and higher concentration of the particles within the channel during material removal. It is expected that the concentration of the particles (between the electrodes) will rise due to their longer dwelling time on the surface of the workpiece during material removal. Furthermore, the particles are also embodied with higher velocity due to the increase of the DC electric field strength.

4.3 Results and discussion on particle effect dependency on the material removal process

It appeared in equation (2.7) that the effect of the abrasive particles has an influence on the electrokinetic effect of the particles for material removal. Experiments were therefore carried out to study the particles effect dependency on the electrokinetic material removal process. Table 4.6 was designed to study the particle effect dependency of the process.

Table 4.6 Experimental table to study the particle effect dependency on the material removal rate

Experiment	Time	Particle size	Concentration of particles	Particle type	DC electric field strength	AC electric field strength (pk-pk)	AC electric field frequency	Fluid velocity
	(min)	(μm)			(kV/cm)	(kV/cm)	(Hz)	(m/s)
Experiment 1 (Fig 4.21)	60	0.5 ~ 1.5	0.01 (g/ml)	Silicon oxide	12.5	50	10	0.40
Experiment 2 (Fig 4.22)	60	1.5	0.001 ~ 0.035 (g/ml)	Silicon oxide	12.5	50	10	0.40
Experiment 3 (Fig 4.25)	60	1.5	0.1 ~ 4.5 (wt%)	Silicon oxide / aluminium oxide	12.5	50	10	0.40
Experiment 4 (Fig 4.26)			0.01 ~ 1.00 (vol%)					
Experiment 5 (Fig 4.27)	15~60		0.01 (g/ml)					

4.3.1 Influence of particle size effect on the material removal rate of the workpiece

Fig 4.21 The influence of particle size on the material removal rate of gold workpiece

It was observed that the material removal rate rose with increasing particle size. Tillet [144] had reported that there is a specific particle size effect that requires increasing abrasive velocity on smaller particle size to achieve material removal of the same effect as that compared to a lower abrasive velocity with a larger particle size. Hence, one would expect the material removal rate of the workpiece to decrease with smaller particle size if the particle velocity is fixed. This is evident in Fig 4.21 where we observed a rise in the material removal rate of the workpiece with increasing particle size. However, it is expected that the material removal rate may reach a certain point after which it will start to decrease. There are a few factors which may influence the decline in the material removal rate with an increase in the particle size. These include:

- A sharp increase of the drag force of the particles with respect to size as compared to the electrokinetic force,
- A decrease in the number of particles in the slurry, and
- Insufficient distance for the particles to pick up adequate speed before collision onto the surface of the workpiece

4.2.2 Influence of particle concentration on the material removal rate of the workpiece

Fig 4.22 The influence of particle concentration on the material removal rate of gold workpiece

A study on the relationship between the material removal rate and the concentration of the abrasive particles in the slurry during the material removal process was carried out during the conduct of the experiments. It was observed from Fig 4.22 that the material removal rate of the particles reached a maximum material removal rate of 2500 Angstrom/Hr before a decrease in the material rate occurred. This could be explained by an illustration of the particles as shown in Fig 4.23.

Fig 4.23 A schematic showing the stacking of the abrasive particles when they are approaching the surface of the workpiece during the material removal process at concentration 0.01 g/ml

Fig 4.23 illustrates the packing of the abrasive particles when they approach the surface of the workpiece during the material removal process. The illustration was drawn after a mathematical calculation (refer to section 5.2 for further details on the calculation) was made to determine the number of layers of the abrasive particles that were packed together when they approached the workpiece during each AC electric field cycle. When the concentration of the abrasive particles is too low (i.e. 0.001 g/ml), only a mono-layer of the abrasive particles approached the surface of the workpiece. However, when the concentration of the abrasive particles was increased, the material removal rate rose. A reason for the rise in the material removal rate was due to the increase in the participation of the abrasive particles during the material removal process. Compounding to this, the abrasive particles were reaching the surface of the workpiece with increasing inertia. This is because the layer of abrasive particles on the surface of the workpiece were “pushed” against it by the incoming particles in the subsequent layers which aided in overcoming the drag force on the layer of particles that were closest to the workpiece. Conversely, when the concentration of the abrasive particles was higher, the particles were unable to

collide onto the surface of the workpiece with sufficient velocity to cause material removal on it. This is because the abrasive particles were not given enough distance to gain sufficient velocity before collision. In addition, when the concentration of the abrasive particles was above 0.025 g/ml, the material removal rate was low as the channels were fully packed with abrasive particles.

4.2.3 Influence of particle type on the material removal rate of the workpiece

Since the material removal mechanism of the electrokinetic process can be considered as a free abrasive machining process, a study was made to determine the performance of the different types of abrasive particles in the slurry on the material removal rate of the process.

According to Table 4.3, silicon oxide and aluminium oxide are amongst the two types of commonly-used abrasive with higher zeta potential in ethanol. Fig 4.24 shows the TEM images of the particles.

Fig 4.24 TEM images of the (a) silicon oxide abrasives (b) aluminium oxide abrasives

It is observed from Fig 4.24 that the silicon oxide abrasive particles are 1.5 μm in diameter and are spherical in shape whilst the aluminium oxide abrasive particles are 1.0~1.5 μm in diameter and are irregular shaped. The zeta potential analyzer was also utilized to determine the sizes and the zeta potentials of both the particles. Table 4.7 lists the characteristics of the particles.

Table 4.7 Characteristics of particles for the study of the influence of particle type on the material removal rate

Factor	Unit	Material	
Workpiece Material		Gold	
Particle		Silicon oxide	Aluminium oxide
Particle size	(microns)	1.5	1.0~1.5
Particle density	(g/cm ³)	~2	~4
Particle zeta potential	(mV)	-64.5	-56.5

Fig 4.25 Influence of the concentration of abrasive particles in the slurry (wt %) on material removal rate

Fig 4.25 shows the influence of the concentration of the particles in the slurry on the material removal rate of the electrokinetic process. In the graph, the material removal curves were plotted against the weight percentage concentration of the particles. It was observed that there is an optimum concentration for maximum material removal for the two types of particles. It was also observed that the maximum material removal rate for the aluminium oxide slurry occurred at approximately 3 wt% concentration as compared to the silicon oxide slurry which occurred at approximately 1.5 wt%.

To further understand the influence of the concentration of the particles on the material removal rate of the electrokinetic process, an attempt was made by plotting the material removal rate of the process against the volume percentage concentration of the abrasive particles in the slurry as shown in Fig 4.26. It was observed that the material removal rate for both of the abrasive particles peaked at approximately the same volume percentage concentration.

Fig 4.26 Influence of the concentration of abrasive particles in the slurry (vol %) on material removal rate

The reason for the aluminium oxide slurry to peak at twice the weight percentage concentration of the silicon oxide slurry was due to the difference in the density of the particles. This is because the density of the aluminium oxide was twice that of the silicon oxide particles.

It was realized that the volume concentration of the particles has a more drastic effect on the material removal rate as compared to the weight percentage concentration of the particles. It was earlier suggested that the material removal process depends on the number of layers of particles that approach the surface of the workpiece during each AC electric field cycle. In this case, the number of layers of particles would be more susceptible to the volume percentage concentration as compared to the weight percentage concentration which was observed during the experiment.

During the experimentation, similar observations were made with respect to section 4.2.2. It was observed that the material removal rate was low when the concentration of the particles was too low. This is because only a mono-layer of the abrasive particles approached the surface of the workpiece at low particle concentration. However, when the concentration of the particles increased, the material removal rate rose. It was suggested that the rise in the material removal rate was due to the increase in the participation of the particles on the material removal process. Furthermore, the particles were reaching the surface of the workpiece with increasing inertia as the layer of particles on the surface of the workpiece are “pushed” against it by the incoming particles in the subsequent layers. This may aid in overcoming the drag force on the layer of particles that were closest to the workpiece. However, when the concentration of the particles was higher, the particles were unable to collide onto the surface of the workpiece with sufficient velocity to cause material removal as the particles were not given enough distance to gain sufficient velocity before collision.

Fig 4.27 Material removal of gold over a process time of 60 minutes with different particles

Fig 4.27 shows the material removal of the electrokinetic material removal process at different time intervals for the respective particles. It was observed that the material removal rates were constant for both types of particles. It was also observed that the material removal rate of the process by utilizing the aluminium oxide particles is slightly higher as compared to the silicon oxide particles. Although one may expect the material removal rate of the process from the aluminium oxide slurry to be much higher than that of the silicon oxide one [118,145], this was not the case according to the results obtained from the experiment. Although aluminium oxide particles are harder and possess sharper edges as compared to the silicon oxide ones, the former did not achieve a much higher material removal rate. A possible reason may be due to the lower zeta potential magnitude which drastically affected the velocity of the particles when they were under the influence of the electrokinetic effect. In addition, the general mean size of the aluminium oxide particles (1~1.5 μm) were smaller to that of the silicon oxide ones (1.5 μm).

4.4 Summary

During the material removal study, a combination of DC and AC electrokinetic effects was proposed. To study the electrokinetic material removal technique, selection of the fabrication methods of the base substrate and the material for the process was undertaken to study the mechanical aspect of the technique. As mentioned earlier, the problem with the setup was that a considerable amount of fluid was leaking out of the channel due to a poor seal between the base substrate and the workpiece/coverglass. This was corrected using PDMS to form the channels.

The initial results showed a noticeable material removal on the workpiece and demonstrated the feasibility of the material removal from the surface of the workpiece. The initial result also showed that the proposed electrokinetic material removal technique was capable of removing material away at the nanometric level. Experiments were designed to further study the effects of the various parameters that could affect the material removal rate on the surface of the material. The effects of the parameters were subsequently showed and discussed.

The material removal mechanism will be further discussed in the next chapter where a model for the material removal technique will be proposed.

Chapter 5

Identification, confirmation and modelling of material removal mechanism

From the results shown in the previous chapter, the mechanism of the electrokinetic material removal appeared to be mainly attributed to the mechanical aspect of the machining. However, a more detailed discussion is made in this chapter to understand more about the process.

In this chapter, a detailed discussion on the identification of the material removal mechanism will be made. In the first section, a model will be introduced to understand the effects of the parameters against the trajectory of the particles in the fluidic channel where material removal rate of the workpiece may be influenced by the trajectory. The identification of the possible material removal mechanism will be subsequently carried out. Following that, modelling of the material removal rate in the electrokinetic material removal process will be proposed in section 5.2 where the calculated and the experimentally obtained material removal rates will be compared. Subsequently, a summary of the chapter will be made as shown in Fig 5.1.

Fig 5.1 Overview of Chapter 5

5.1 Identification and confirmation of material removal mechanism

To understand the relationship between the material removal rate of the workpiece and the different parameters (as discussed in Chapter 4) that might affect it, an identification of the material removal mechanism is necessary.

It is realized from the literature that the minimum energy that is required to enable material removal from the gold workpiece is 3.5~4.0 eV where the value of the energy corresponds to the gold metallic bonding energy [146]. As mentioned in chapter 2, there are several ways to achieve material removal. The methods of removing the material from the surface may be due to the following mechanisms:

1. Mechanical method (kinetic energy)
2. Non-mechanical methods
 - (a) Chemical dissolution
 - (b) Galvanic corrosion
 - (c) Pitting corrosion
 - (d) Electrical arcing
 - (e) Stress corrosion cracking

An initial calculation had to be carried out to understand if the material removal was a mechanical or a non-mechanical process before a suitable model could be applied to it to analyze the mechanism. A flow chart for the identification of the mechanism is shown in Fig 5.2 which illustrates the flow of actions that are to be carried out in the study of material removal.

Fig 5.2 Flowchart for the identification of the material removal mechanism

To calculate the minimum velocity of the abrasive particles to cause material removal mechanically, the kinetic energy of the abrasive particles was equated to the metallic bonding energy of gold:

$$K.E = \frac{1}{2} m_p V_p^2 \quad (5.1)$$

where m_p is the mass of the particle and V_p is the net velocity of the particle

It was realized from the calculation that the minimum velocity of the abrasive particles (1.5 μm in diameter) to break the metallic gold bonding was about 0.0165 m/s (16.5 mm/s).

5.1.1 Modelling on the trajectory of the particles during electrokinetic material removal process

Modelling on the trajectory of the particles during the material removal process was performed to study if the particles were sufficiently energetic enough to achieve material removal mechanically during the process.

There are several forces that act on the abrasive particle in the slurry, along the channel, during the material removal process. The main influences that act on the abrasive particles to cause particle motion within the fluid are dominated by both the electrokinetic and hydrodynamic effects in the Y and X direction respectively as shown in Fig 5.3. Fig 5.3 shows the electrokinetic and the hydrodynamic effects on the particle during impingement of workpiece for material removal. By varying the ratio of the electrokinetic effect to the hydrodynamic effect on the particle, the velocity and the angle of impingement of the particle to the surface of the workpiece are altered.

Fig 5.3 Influences of the main effects acting on the particle during the material removal process

The main forces that act on the abrasive particle due to the electrokinetic and hydrodynamic effects cause motion of the particle in the Y and X direction respectively. However, the primary focus for the determination of the trajectory is to find out the net resultant velocity of the particle during impingement. The mechanism of the material removal process is proclaimed as a mechanical one only when the net resultant velocity of the abrasive particles is greater than that of the metallic bonds of the workpiece. The forces that act on the abrasive particle due to the electrokinetic and hydrodynamic effects will be covered in a more detailed manner in the following subsections.

In order to model the trajectory of the particles during the material removal process, both mathematical model and simulation were used. The mathematical model (using MATLAB[®]) and multi-physics simulation (using COMSOL[®]) were performed to study the electrokinetic and the hydrodynamic effects on the trajectory of the particles in the slurry during the material removal process respectively.

5.1.1.1 Electrokinetic effect on the trajectory of the particle

The free body force diagram to model the electrokinetic effect on the trajectory of the particle in the Y direction is shown in Fig 5.4. Altogether, there are 4 main forces that affect the trajectory of the particle in the Y direction. They are namely: (a) $F_{E(DC+AC)}$: electrokinetic force due to the DC and AC electric field (b) F_B : buoyancy force (c) F_G : gravitational force and (d) F_{Drag_y} : drag force acting against the motion of the particle in the fluid in the Y direction.

Fig 5.4 Free body diagram of the electrokinetic effect acting on the particle during the material removal process

The force balance in the Y direction can be written as:

$$\sum F_Y = m_p a_y = m_p \frac{V_y}{dt} = m_p \frac{d^2 y}{dt^2} = F_{E(DC+AC)} + F_B - F_G - F_{Drag_y} \quad (5.2)$$

where F_Y refers to the forces in the Y direction, m_p refers to the mass of the abrasive particles, a_y and V_y refers to the acceleration and velocity of the particle in the Y direction respectively

According to equation (5.2), the first term on the right hand side, $F_{E(DC+AC)}$, refers to the electrokinetic force where its surface charge was given previously in equation (2.7). Due to the fact that a dielectric fluid (which has a very low electrolyte concentration) was used during the electrokinetic material removal process, $\kappa \rightarrow 0$. This reduces equation (2.7) to:

$$F_E = [4\pi\epsilon_r\epsilon_0 r\zeta] E \quad (5.3)$$

where r is the radius of the particle, ϵ_r is the relative permittivity, ϵ_0 is the permittivity of vacuum, ζ is the zeta potential of the particle and E is the external electric field that is acting on the spherical particle

Due to the influence of both the DC and AC electric field acting on the abrasive particles, the overall electric field, E , during the material removal process can be represented as:

$$E = E_{DC} + E_{AC} \quad (5.4)$$

where E_{DC} and E_{AC} refers to the DC and AC electric field respectively

The DC component of the electric field is given by:

$$E_{DC} = \frac{V_{DC}}{H} \quad (5.5)$$

where V_{DC} is the DC voltage applied and H is the height of the channel

The AC component of the electric field is given by:

$$E_{AC} = \frac{V_{AC} \sin(2\pi ft)}{H} \quad (5.6)$$

where t is time, V_{AC} is the amplitude and f is the frequency of the AC voltage applied

Substituting equations (5.4) - (5.6) into equation (5.3) gives:

$$F_{E(DC+AC)} = [4\pi\epsilon_r\epsilon_0a\zeta] \left(\frac{V_{DC}}{H} + \frac{V_{AC} \sin(2\pi ft)}{H} \right) \quad (5.7)$$

In addition, a correction factor $\sigma(h)$ is also attached to the electrokinetic force expression for a sphere undergoing electrophoresis; it is associated with the differences in flow patterns between sedimenting vs electrophoretically driven spheres [147]. This gives the electrokinetic force the following expression

$$F_{E(DC+AC)} = F_E \cdot \sigma(h) = 4\pi r\epsilon_r\epsilon_0\zeta \left[\left(\frac{V_{AC} \sin(2\pi ft)}{H} \right) + \left(\frac{V_{DC}}{H} \right) \right] \left[\frac{h+1.554r}{h+0.3r} \right] \quad (5.8)$$

where r is the radius of the abrasive particle, ϵ_r is the permittivity of the fluid, ϵ_0 is the permittivity of vacuum, ζ is the zeta potential of the abrasive particle, V_{AC} is the AC voltage, f is the frequency of the electric field, H is the distance between the base substrate and the workpiece and h is the instantaneous thickness of the gap between the planar wall surface and the closest point on the particle

The second term on the right hand side of equation (5.2) refers to the buoyancy force of the fluid that is acting against the particle:

$$\begin{aligned} F_B &= V \rho_f g \\ F_B &= \left(\frac{4}{3} \pi r^3 \right) \rho_f g \end{aligned} \quad (5.9)$$

where ρ_f is the density of the fluid

The third term on the right hand side of equation (5.2) refers to the gravitational pull of the particle:

$$\begin{aligned} F_G &= V \rho_p g \\ F_G &= \left(\frac{4}{3} \pi r^3 \right) \rho_p g \end{aligned} \quad (5.10)$$

where ρ_p is the density of the particle

The fourth term on the right hand side refers to the drag force of the particle that takes into the consideration of the wall correction factor, $\alpha(h)$ [147], which gives the drag force expression as:

$$F_{Drag_y} = \alpha(h) C_D \left(\frac{dy}{dt} \right) = \left[\frac{6h^2 + 9rh + 2r^2}{6h^2 + 2rh} \right] (6\pi r \eta) \left(\frac{dy}{dt} \right) \quad (5.11)$$

where η is the viscosity of the fluid and h is the instantaneous thickness of the gap between the planar wall surface and the closest point on the particle

By substituting equations (5.8)-(5.11) into equation (5.2), the complete force balance in the Y direction is formed.

The equation of motion (equation (5.2)) based on Newton second law was modelled to understand the effect of the electrokinetic phenomenon of the abrasive particles on the material removal mechanism. The second order ordinary differential equation was formed (by substituting equations (5.8)-(5.11) into equation (5.2)), to model the trajectory of the particle. During the modelling, it was assumed that the shape of the abrasive particles was spherical and the interactions among the particles were ignored.

The Runge-Kutta method was used to solve the equation for the electrokinetic motion of the particle. To simplify the equation, the second order differential equation was rewritten into two first order differential equations. MATLAB[®] (version 7 R14, Math Works) was then used to solve the differential equation for the vertical direction of the particle.

The modelling conditions that were utilized to show the trajectory of the particles to understand their motion in the slurry at various conditions during the material removal process are shown in Table 5.1.

Table 5.1 Modelling conditions for the electrokinetic material removal process

Parameters	Conditions
Particle	SiO ₂ Radius, $r = 0.75 \mu\text{m}$ Mass, $m_p = 3.9 \times 10^{-15} \text{ kg}$ Zeta potential = - 64.5 mV Density, $\rho_p = 2.20 \text{ g/cm}^3$
Machining fluid	Ethanol Dielectric constant, $\epsilon_r = 24.3$ Viscosity, $\eta = 0.9 \text{ mPas}$ Density, $\rho_p = 0.789 \text{ g/cm}^3$
Workpiece	500 nm gold on 1 μm thick of silicon dioxide
Electric field	DC Bias, $V_{\text{DC}} = 12.5 \text{ kV/cm}$ AC electric field (pk-pk), $V_{\text{AC}} = 50 \text{ kV/cm}$ Frequency = 1000 Hz
Fluidic channel	Length = 30 mm Width = 500 μm Height = 20 μm

Fig 5.5 (a) shows the mathematical trajectory of the particle at the centre of the channel when it was under the influence of AC electric field (pk-pk) at 50 kV/cm with frequency, $f = 1000 \text{ Hz}$. It was observed that the particle was oscillating about the centre of the channel. However, when the particle was subjected to an AC electric field with a DC bias as shown in Fig 5.5 (b), it was observed that the particle began to move towards the surface of the workpiece. The particle was expected to move towards the surface of the workpiece as the particle was negatively charged while the workpiece was positively biased. When the frequency was reduced, the particle approached the surface of the workpiece with higher velocity and dwelled onto it upon reaching as shown in Fig 5.5 (c) and (d).

Fig 5.5 MATLAB® modelling on the trajectories of the particle (a) when the particle is subjected to AC electric field only (b) when the particle is subjected to AC electric field with a DC bias (c) when the particle is subjected to a lower AC electric field frequency with a DC bias (d) when the particle is subjected to an even lower AC electric field frequency with a DC bias

During the MATLAB[®] modelling, other magnitudes of the AC electric field strength and frequency were undertaken to understand the trajectory of the particles. Velocity studies on the trajectory of the particles were also carried out to further understand the material removal mechanism. Modelling results showed that the velocities in the vertical direction of the particles were in the range of around 10 mm/s to 50 mm/s during the experimental processes that were carried out in Table 4.4.

5.1.1.2 Hydrodynamic effect on the trajectory of the particle

Besides the influence of the electrokinetic effect on the material removal, the hydrodynamic effect of the fluidic flow is also responsible for the material removal mechanism on the workpiece. Therefore, a study into hydrodynamic effect is necessary to understand if the fluid velocity was high enough to drag the particles along the surface of the workpiece to cause material removal.

Fig 5.6 shows the free body diagram of the abrasive particle in the X direction. There are 2 main forces that act on the particle. They are namely: (a) F_{pump} : the pumping force of the fluid acting on the particle and (b) F_{Drag_x} : the drag force acting against the motion of the particle in the X direction.

Fig 5.6 Free body diagram of the hydrodynamic effect acting on the particle during the material removal process

A study on the Reynolds number was carried out to determine the flow of the fluid across the channel where it is given by [148]:

$$\text{Re} = \frac{\rho_f \cdot U \cdot D_H}{\eta} \quad (5.12)$$

where U is the general velocity of the fluid flow and D_H is the hydraulic diameter of the channel.

As the channel is a rectangular one, the hydraulic diameter [148] of the channel is expressed as:

$$D_H = \frac{4A}{P} = \frac{4w \cdot H}{2(w + H)} \quad (5.13)$$

where A is the cross sectional area of the channel, P is the perimeter of the cross section of the channel, w is the width of the channel and H is the height of the channel

The Reynolds number of the flow across the channel was calculated by substituting equation (5.13) into (5.12). By inputting the experimental values according to Table 4.4, the Reynolds number was determined to fall within the laminar flow regime where $\text{Re} < 2300$ [149]. The calculated Re was determined mathematically to fall within the range of 3~25.

As the condition during the material removal process involves in a low Reynolds number, it was assumed that the flow across the channel was fully developed and was in steady state condition. When the flow is in steady state, it can be suggested that the particle in the slurry does not encounter acceleration in the flow of the slurry, i.e. $\sum F_x = 0$. It is reasonable to assume that the abrasive particles move in the same velocity as the slurry flow [150].

During the experiments, the slurry was pumped into the channel at a constant flow rate, Q where it is given by [149]:

$$Q = AU$$

$$\frac{Q}{w} = -\frac{1}{12\eta} \left(\frac{\partial p_f}{\partial L} \right) H^3 \quad (5.14)$$

where Q is the flow rate of the fluid, A is the cross-sectional area of the channel, U is the general fluid velocity of the fluid, w is the width of the channel, p_f is the pressure of the flow, L is the length of the channel, η is the viscosity of the fluid and H is the height of the channel

To study the localized velocity of the particle at the different position of the channel, a velocity profile of the fluid within the fluidic channel had to be determined [149]:

$$u = \frac{H^2}{2\eta} \left(\frac{\partial p_f}{\partial L} \right) \left[\left(\frac{y'}{H} \right)^2 - \frac{1}{4} \right] \quad (5.15)$$

where y' is the distance of the localized element of the fluid from the centre of the separation between the two electrodes

Since the abrasive particle is travelling at the same velocity of the slurry flow, the velocity of the particle, V_x can be represented by substituting equation (5.14) into (5.15) as:

$$V_x = u = 6U \left[\frac{1}{4} - \left(\frac{y'}{H} \right)^2 \right] \quad (5.16)$$

A simulation for the velocity profile of the fluid/particles was undertaken by using a commercial multi-physics software (COMSOL[®] software). The results from the simulation are shown in Fig 5.7. From the analysis, it was realized that the velocity of the

fluid that was acting on the centre of the particle was approximately twenty percent of the general fluid velocity as shown in Fig 5.7 (b).

Fig 5.7 COMSOL® simulation on the velocity profile of the particle (a) a 2-D simulation plot of the fluid velocity (b) a 1-D simulation of the velocity profile of the fluidic channel. Both simulations were performed with the general fluid velocity of the internal flow as 0.2 m/s

5.1.2 Dominant material removal mechanism during process

From the calculations according to equations (5.2) and (5.16), the net velocity of the abrasive particle can be determined where:

$$V_p = \sqrt{V_x^2 + V_y^2} \quad (5.17)$$

$$\alpha_p = \tan^{-1} \left(\frac{V_y}{V_x} \right) \quad (5.18)$$

Based on calculations for the determination of the net velocity of the abrasive particles according to the conditions in Table 4.4, it was realized that the minimum velocity of the abrasive particles at the slowest flow rate of the fluid are much faster than the minimum velocity to break the metallic gold bonds (>16.5 mm/s). Therefore, it was concluded that the most likely mechanism is the mechanical one.

Other material removal mechanisms were regarded as insignificant as there were insufficient evidence to suggest their presence and influence. Some of the possible material removal mechanisms that could be present in the material removal include electrical arcing and galvanic corrosion. However, EDM phenomenon could not be identified as the material removal process as there was insufficient presence of craters to suggest so [125]. Galvanic corrosion could not be the main mechanism also as the fluid that was utilized during the process was a dielectric one. Stress corrosion cracking effect was not expected as there was no blister formation on the surface of the gold substrate as well. Chemical reactions were also unlikely as there was no formation of aqueous or liquid compounds during the material removal process. This consequently led us to suggest that the mechanical material removal mechanism to be the most possible method as the net resultant velocity of the particles exceeds the energy required to break the metallic bond of the atoms in the workpiece. As the energy of the particles is believed to be only a few times of that to break the gold metallic bonds, it is suspected that the material removal process is similar to EEM.

To further study the material removal mechanism of the process, experiments were carried out according to the various conditions that were illustrated in Fig 4.2. where the abrasive particles were subjected to fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only and (d) AC electric field with a DC bias. The outcomes of the material removal on the gold workpieces under these conditions over a period of 1 hour are shown in Fig 5.8.

Fig 5.8 shows the surface plots of the workpieces with different level of material removal under the various influences of electrokinetic and hydrodynamic effects. The raw measurements of the surface plots were obtained by using the white light interferometer before a surface analysis software (Mountains[®] from Digital Surf) was utilized to post-process the data for comparisons.

Fig 5.8 The material removal on the gold workpiece when the abrasive particles in the slurry are under the influences of fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only (d) AC electric field with a DC bias (e) AC electric field with a DC bias (without abrasive particles). (Silicon oxide particle size: $1.5\mu\text{m}$, particle concentration: 0.01g/ml , fluid velocity: 0.4 m/s , DC electric field strength: 12.5 kV/cm , AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

A quantification of the material removal due to the conditions (a)-(e) according to Fig 5.8 is shown in Fig 5.9.

Fig 5.9 Comparisons of the material removal on the gold workpieces when the abrasive particles in the slurry are under the influences of fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only (d) AC electric field with a DC bias (e) AC electric field with a DC bias (without abrasive particles). (Silicon oxide particle size: $1.5\mu\text{m}$, particle concentration: 0.01g/ml , fluid velocity: 0.4 m/s , DC electric field strength: 12.5 kV/cm , AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

From Fig 5.9, it was observed that there was no material removal when the silicon oxide abrasive particles were subjected to the fluid flow only. However, substantial material removal was observed when the particles were subjected to fluid flow and AC electric field. When the particles were under the influence of the fluid flow and DC electric field,

negligible material removal was recorded. It was only with the presence of the fluid flow and AC electric field with a DC bias that the particles removed the most material from the surface of the gold workpiece. An additional condition to investigate the material removal from the workpiece when no particles were present was included (condition (e) according to Fig 5.8 and 5.9). This was to confirm if the material removal mechanism was indeed a mechanically dominant one. Results showed that the material removal was slight. This proved the hypothesis that the mechanical material removal as the dominant mechanism holds. The most likely reason for the material removal under condition (e) was due to the effect of the electrochemical dissolution of gold when the electrodes were subjected to the electric field [151]. Nonetheless, the material removal due to the electrochemical dissolution of gold was subtle and could be considered insignificant as compared to that of the mechanical material removal mechanism of the electrokinetic material removal process.

During the electrokinetic material removal process, the material removal on the gold was believed to be assisted by electrochemical dissolution as the metallic bonds between the atoms may have been weakened to a certain extent [151]. This led to the possibility of requiring lesser mechanical energy to remove the gold atoms from the surface of the workpiece.

To further understand the mechanical material removal mechanism of the process, observations were made on the abrasive particles after the material removal process.

5.1.2.1 Observation of the abrasive particle before and after the material removal process

The zeta potential analyzer, field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the abrasive particles before and after the electrokinetic material removal process.

The zeta potential analyzer was used to quantify and compare the particle size of the abrasives. Table 5.2 illustrates the particle size of the abrasive particles before and after the material removal process.

Table 5.2 Characteristics of the abrasive particles before and after the electrokinetic material removal process

	Before material removal process	After material removal process
Average size (in μm)	1.3 - 1.7	1.4 - 1.7

In terms of the size of the abrasive particles, it was observed (from Table 5.2) that there was no noticeable increase of particles size to suggest material transfer from the gold workpiece to the abrasive particles. However, it can be concluded that the fragmentation of the particles after the material removal process may not be possible as the abrasive particle sizes remained the same. To further validate that the particles were not fragmented, the FESEM was used for further analyses.

Fig 5.10 FESEM micrographs of the silicon oxide particles collected (a) before the process (b) after the process (c) after the process at higher magnification

Fig 5.10 shows the micrograph of the particles before and after the electrokinetic material removal process. It was observed that the particles were uniformly $1.5\ \mu\text{m}$ in size and showed no signs of fragmentation after the material removal process. However, evidence of material adhering onto the particles were observed where gentle bumps on the surface of the particles were seen. Fig 5.10 (c) shows clearly the adhesion of the material.

An XPS analysis was performed on the particles that were collected after the electrokinetic material removal process. Data of the analysis is shown in Table 5.3.

Table 5.3 XPS analysis of the abrasive particles before and after the electrokinetic material removal process

Element	Position Binding energy	Full with at half maximum (FWHM)	Raw Area	Relative sensitivity factor (RSF)	Atomic mass	Atomic concentration	Mass concentration
	(eV)	(eV)	(cps)			(%)	(%)
Before process							
O 1s	531.9	1.458	44982.7	0.780	15.999	45.99	41.20
C 1s1	284.1	1.230	7294.6	0.278	12.011	24.36	16.38
C 1s2	285.5	1.646	1260.5	0.278	12.011	4.21	2.83
C 1s3	288.6	0.974	131.5	0.278	12.011	0.44	0.29
Si 2p	102.8	1.544	7355.4	0.328	28.086	25.00	39.30
Au 4f7/2	-	-	-	-	-	0.00	0.00
Au 4f5/2	-	-	-	-	-	0.00	0.00
Total concentration %	-	-	-	-	-	100.00	100.00
After process							
O 1s	532.0	1.708	28648.9	0.780	15.999	26.37	28.53
C 1s1	284.1	1.382	13374.1	0.278	12.011	40.20	32.66
C 1s2	285.5	1.619	6615.3	0.278	12.011	19.87	16.14
C 1s3	288.1	1.224	1081.4	0.278	12.011	3.24	2.64
Si 2p	102.9	1.563	3367.5	0.328	28.086	10.29	19.53
Au 4f7/2	84.0	1.727	139.6	0.250	196.967	0.02	0.31
Au 4f5/2	87.7	1.843	87.0	0.250	196.967	0.01	0.19
Total concentration %	-	-	-	-	-	100.00	100.00

Results from Table 5.3 shows that the material that was adhering to the particles was gold. Further analysis of the XPS result on the gold element that resided on the silicon oxide abrasive particles, as shown in Fig 5.11, was made and suggested that the gold material adhering onto the surface of the particles was that of metallic gold instead of oxide. The gold element (Au 4f 7/2) peaked at around 84.0 eV which suggested the gold element to be metallic [152-154]. As the gold element in Fig 5.11 did not exhibit shoulders, it was believed that gold oxide was not possible [153]. Therefore, this further suggested that the material removal during the process was that of adhesion as chemical reaction between the gold workpiece and the silicon oxide particles to form gold oxide was not visible.

Fig 5.11 XPS spectrum (for gold) recorded on the silicon oxide abrasive particles after the electrokinetic material removal process

5.2 Modelling of material removal rate in the electrokinetic material removal process

The preliminary calculations and observations led us to suggest that the mechanical mechanism was the most prevalent method for the material removal as the net resultant velocity of the particles far exceeded the energy to break the metallic bonds of the workpiece. Consequently, several material removal mechanisms were studied to understand how they could be applied to describe the material removal of the process.

After referring to several material removal mechanisms, it is believed that the electrokinetic material removal mechanism is somehow analogous to that of the EEM technique as they hold certain similarities. Both the EEM and the electrokinetic techniques use micro/nano particles in slurries as abrasives to achieve material removal on the workpiece mechanically by removing material at the nanometric level. In addition, both of the techniques are non-contact micromachining methods. This resulted in the belief that a model similar to the EEM technique could be used to apply for the material mechanism of the electrokinetic material removal technique. Both Mori [68] and Kim [111] have reported that the material removal mechanism of EEM could be modelled by both the atomic material removal model and erosion material removal mechanism (erosion model) respectively. Due to this, both models were taken into consideration to account for the electrokinetic material removal mechanism. Ultimately, the erosion model was chosen as it was able to take issues such as the angle of impingement, particle concentration and velocity into consideration which could give a more robust model for the understanding of the electrokinetic material removal process. On the other hand, the molecular dynamics simulation that studies the atomic material removal model might be too focused into looking at the molecular interactions between the abrasive particles and might not be robust enough to account for the entire process for the material removal.

It was evident from Fig 4.11 and 4.12 that the particles were impinging onto the surface of the workpiece during the process. The process appeared to be analogous to that of the

erosion model except that the fluid in the erosion process was air whereas the fluid for the electrokinetic material removal process was that of a liquid.

As such, the established Finnie model [112] was used to study the material removal of the workpiece due to the electrokinetic material removal process, where

$$V_0 = \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p}\right)} \cdot \frac{2}{P} \left[\sin 2\alpha_p - 2 \frac{\sin^2 \alpha_p}{P} \right], \quad \alpha_p \leq \hat{\alpha}_p \quad (5.19)$$

$$V_0 = \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p}\right)} \left[\cos^2 \alpha_p \right], \quad \alpha_p \geq \hat{\alpha}_p \quad (5.20)$$

$$\hat{\alpha}_p = \tan^{-1} \left(\frac{P}{2} \right) \quad (5.21)$$

$$P = \frac{K}{1 + \frac{m_p r^2}{I_p}} \quad (5.22)$$

and

$$I_p = \frac{m_p r^2}{3} \quad (5.23)$$

where V_0 is the volume of the material removal, C is a constant that is related to the amount of the particles impacting onto the surface of the workpiece, m_p is the mass of the eroding particle, V_p is the flow speed of the particle, n is an exponential value (in the region where $n \approx 2$), α_p is the angle of impingement, r is the radius of the particle, I_p is the moment of inertia of the particle about its centre of gravity, K is the ratio of the vertical to the horizontal force components acting on the impacting particle, p (which is

related to hardness) is the flow pressure between the abrasive and the surface of the workpiece, $\hat{\alpha}_p$ is the angle of impingement for maximum material removal and P is a constant that is related to the coefficient of friction between the abrasive particles and the surface of the workpiece

As shown in Fig 4.22, the concentration of the abrasive particles plays an important part in the material removal of the electrokinetic material removal process. The importance of the role of the concentration of the abrasive particles was highlighted in the EEM [111,155] and erosion process [112]. In EEM, Kim [111] related higher material removal with increased participation of particles colliding with the surface of the workpiece. Similarly, higher material removal, with increased concentration of particles, was also observed and modelled in the erosion experiment. This is evident where the volume of the material removal was associated with the total mass of the eroding particles. This meant that the concentration of the particles was considered during the modelling process. The effect of abrasive concentration was also observed in the chemical mechanical polishing process and was deemed to be one of the crucial factors for the material removal rate of the process [54,156]. In fact, the concentration of particles has a notable impact in the material removal rate of free abrasive machining techniques.

5.2.1 Incorporation of particle concentration effect on material removal rate model

It appeared, in the previous section, that the erosion model was the most appropriate one to account for the material removal rate of the electrokinetic material removal process. However, the model had to be slightly modified to account for the material removal rate of the electrokinetic material removal process. An additional function, relating to the concentration of the particles participating in the impingements with the surface of the workpiece within the channel during each cycle, had to be added to the existing erosion model in equations (5.19) & (5.20) to more accurately account for the material removal rate of the process in 1 hour (material removal rate (MRR)).

With the incorporation of the concentration effect on the material removal model, the equations can be expressed as:

$$MRR = f(conc) \cdot \frac{1}{t_{process}} \cdot \left\{ \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p} \right)} \cdot \frac{2}{P} \cdot \left[\sin 2\alpha_p - 2 \frac{\sin^2 \alpha_p}{P} \right] \right\}, \quad \alpha_p \leq \hat{\alpha}_p \quad (5.24)$$

$$MRR = f(conc) \cdot \frac{1}{t_{process}} \cdot \left\{ \frac{Cm_p V_p^n}{4p \left(1 + \frac{m_p r^2}{I_p} \right)} \cdot \left[\cos^2 \alpha_p \right] \right\}, \quad \alpha_p \geq \hat{\alpha}_p \quad (5.25)$$

where MRR is the material removal rate of the electrokinetic material removal process and $f(conc)$ is a function relating to the effect of the concentration of the abrasive particles on the material removal rate of the process and $t_{process}$ is the time taken for the material removal process.

$f(conc)$ is a normalised function that was derived empirically. The function was created by normalising the material removal rate at different abrasive concentration in the slurry with that of the maximum material removal rate corresponding to the optimum angle, $\hat{\alpha}_p$ (refer to later part of this section for further details).

It should be noted that the concentration of the abrasive particles in the slurry within the channel during the material removal process is dissimilar to that of the original concentration of abrasive particles in the slurry (where the concentration of the particles in the slurry was 0.01 g/ml for all of the experiments carried out in Table 4.4). In fact, the concentration of the abrasive particles during the material removal process, with the presence of the electric field, was much higher than without the presence of the electric field. This is because the particles in the slurry, under the influence of the electric field, were dwelling (trapped) onto the surface of the workpiece (or within the channel) during each cyclic collision and garnered a tremendous increase in the concentration of abrasive particles. It was tested experimentally that the abrasive particles clogged up the entire channel when the concentration of the abrasive particles exceeded a concentration of 0.025 g/ml. This suggested that the channel was entirely filled with the abrasive particles at 0.025 g/ml concentration. This also led to the assumption that material removal was not achieved by particle impingement with slurry concentration beyond 0.025 g/ml. Rather, material removal with slurry concentration beyond 0.025 g/ml would be referred as material removal due to frictional wear with the surface of the workpiece.

As mentioned earlier on, it was suggested that the channel, at 0.025 g/ml concentration, was fully clogged with particles. Since the height of the channel was 20 μm with the abrasive particles being 1.5 μm in diameter, it would constitute to a total of approximately 13-14 layers of particles being stacked on top of one another throughout the channel before being choked with these abrasives particles.

Due to the dramatic increase in the concentration of the abrasive particles in the channel under the influence of the electrokinetic effect, an expression was suggested to link the

number of layers of stacked abrasive particles throughout the channel in the slurry under the effect, during the material removal process, with that of the original concentration.

The relationship can be expressed as:

$$N_{\text{during process}} = \frac{N_{\text{particles in each cycle}} \cdot N_{\text{cycle}} \cdot \eta_{\text{efficiency_trapping}}}{N_{\text{particles in each layer}}} \quad (5.26)$$

where $N_{\text{during process}}$ is the number of layers of stacked abrasive particles throughout the channel under the electrokinetic effect during the material removal process, $N_{\text{particles in each cycle}}$ is the number of particles in each cycle introduced into the channel, N_{cycle} is the number of cycles each particle undergoes from the entry to the exit of the channel, $\eta_{\text{efficiency_trapping}}$ is the trapping efficiency of the particles during each cyclic collision with the surface of the workpiece and $N_{\text{particles in each layer}}$ is the number of particles in one layer across the channel.

In equation (5.26), $N_{\text{during process}}$ is calculated by multiplying $N_{\text{particles in each cycle}}$ with N_{cycle} and $\eta_{\text{efficiency_trapping}}$ before dividing the product with $N_{\text{particles in each layer}}$. $N_{\text{particles in each cycle}}$ is multiplied with N_{cycle} so that the number of particles throughout all the cycles within the channel is obtained. The product of $N_{\text{particles in each cycle}}$ and N_{cycle} is then multiplied with that of $\eta_{\text{efficiency_trapping}}$ so that a realistic number of the particles throughout the entire channel from the inlet to the outlet of the channel can be calculated. In order to determine $N_{\text{during process}}$, the product of $N_{\text{particles in each cycle}}$, N_{cycle} and $\eta_{\text{efficiency_trapping}}$ is divided by that of $N_{\text{particles in each layer}}$ such that the number of layers of stacked abrasive particles throughout the channel under the electrokinetic effect during the material removal process can be attained.

$N_{\text{particles in each cycle}}$ is obtained by multiplying the concentration of the particles in the slurry upon preparation before the material removal process, $Conc_{\text{original}}$, with the calculated

volume of the channel travelled by the moving and trapped abrasive particles during each cycle, $Vol_{channel \text{ in each cycle }}$, divided by the mass of a single abrasive particle, m_p . As such, $N_{particles \text{ in each cycle }}$ can be expressed as:

$$N_{particles \text{ in each cycle }} = \frac{Conc_{original} . Vol_{channel \text{ in each cycle }}}{m_p} \quad (5.27)$$

$$Vol_{channel \text{ in each cycle }} = w.H.U.(t_p + t_{dwelling \text{ time of the abrasive particles on workpiece }}) \quad (5.28)$$

$$t_{dwelling \text{ time of the abrasive particles on workpiece }} = \left[\frac{(T/4) - t_p}{(T/4)} \right] . T \quad (5.29)$$

where $Conc_{original}$ is the concentration of the particles in the slurry upon preparation before the material removal process, $Vol_{channel \text{ in each cycle }}$ is the supposed volume of the channel travelled by the trapped abrasive particles during each cycle, t_p is the time taken for the abrasive particle to reach onto the surface of the workpiece during each cyclic collision, $t_{dwelling \text{ time of the abrasive particles on workpiece }}$ is the dwelling time of the abrasive particles on the surface of the workpiece and T is the period of each oscillation.

For equation (5.29), it was assumed that the abrasive particles in the channel went through a sinusoidal cycle during each period. Therefore, a quarter of the cyclic oscillation was considered and compared with t_p to obtain a time ratio with that of T (where there are evidence (Fig 4.12) that the abrasive particles dwell on the surface of the workpiece over a period of time before being pulled in the opposite direction during each cyclic oscillation). A schematic to show the consideration of t_p with that of T is shown in Fig 5.12. The ratio of t_p with that of T was assumed to be consistent throughout the sinusoidal cycle during each period. $t_{dwelling \text{ time of the abrasive particles on workpiece }}$ was then obtained by multiplying the ratio with T .

Fig 5.12 Schematic illustrating (a) the trajectory of the abrasive particle with respect to time which shows the relationship of t_p with that of T (b) the position of the abrasive particle at different time intervals (with the same time intervals as (a))

In order to determine the number of cycles each particle undergoes from the entry to the exit of the channel, N_{cycle} was calculated by dividing the length of the channel, L , by the distance travelled by the abrasive particles during each cycle (by multiplying t_p with U). Assuming the entire channel is usually half-filled with abrasive particles (based on experimental results where the abrasive particles would clog up the channel beyond $Conc_{original} = 0.025\text{g/ml}$), each particle would experience an average of $2 t_p$ during each oscillation cycle. Therefore, the number of cycles each particle undergoes from the entry to the exit of the channel, N_{cycle} , can be expressed as:

$$N_{cycle} = \frac{L}{2t_p U} \quad (5.30)$$

During the calculation of $N_{during\ process}$, the trapping efficiency of the particles during each cyclic collision with the surface of the workpiece, $\eta_{efficiency_trapping}$, has to be carefully considered. This is such that a realistic number of the particles throughout the entire channel from the inlet to the outlet of the channel can be calculated. As the effect of both V_x and V_y may influence the trapping efficiency of the particles during each cyclic collision with the surface of the workpiece, a relationship between $\eta_{efficiency_trapping}$, V_x and V_y has to be established.

Camp [157,158] previously expressed the trapping efficiency of the settling particles within a reservoir as:

$$\eta_{efficiency_trapping_reservoir} = \left(\frac{V_s}{V_c} \right) \quad (5.31)$$

where $\eta_{\text{efficiency_trapping_reservoir}}$ is the trapping efficiency of the settling particles in a reservoir, V_s is the settling velocity of the particle and V_c is the critical settling velocity of a particle just removed or deposited before flowing out.

In the context of the trapping efficiency for the particles during each cyclic collision in the electrokinetic material removal process, the expression may be presented as:

$$\eta_{\text{efficiency_trapping}} \propto \left(\frac{V_y}{V_x} \right) \quad (5.32)$$

where $\eta_{\text{efficiency_trapping}}$ is the trapping efficiency of the particles during each cyclic collision with the surface of the workpiece, V_y is the velocity of the particle due to the electrokinetic effect of the particle and V_x is the velocity due to the hydrodynamic effect of the particle.

V_x may be considered as a criterion for the trapping of the particle just removed or deposited before flowing out as it provides the energy for the particle to move out of the channel. However, it should be noted that equation (5.32) holds true for $V_y < k_1 V_x$, and

$\frac{V_y}{V_x} = 1$ when $V_y \geq k_1 V_x$ (where k_1 is an arbitrary constant). For the instance in

$\eta_{\text{efficiency_trapping}}$, k_1 can be considered to be approximated to 1, based on the dimension of the abrasive particles (spherical in shape). If $V_y < V_x$, it can be considered that $\eta_{\text{efficiency_trapping}} < 1$ as the particles have sufficient room to project onto the surface of the workpiece/electrode. However, when $V_y \geq V_x$, it can be considered that $\eta_{\text{efficiency_trapping}} = 1$ as further increase in V_y would only ensure that all the abrasive particles in the channel would dwell onto the surface of the workpiece/electrode. A schematic is shown in Fig 5.13 to further illustrate the consideration of $k_1 \approx 1$.

Fig 5.13 Schematic showing the consideration for the approximation of k_1 where (a) $V_y \geq V_x$ and (b) $V_y < V_x$ ((a) and (b) considers the same time intervals)

To approximate the number of particles in one layer across the channel, $N_{particles\ in\ each\ layer}$, the surface area of the exposed area to the slurry can be divided by that of the area of the particles as shown in Fig 5.14 to obtain it.

Fig 5.14 Schematic showing the consideration of the dimensions of the channel and the abrasive particles size for the approximation of the number of particles in one layer of the channel

Therefore, $N_{particles\ in\ each\ layer}$ can be approximated as:

$$N_{particles\ in\ each\ layer} = \frac{L.w}{4r^2} \quad (5.33)$$

Substituting equations (5.27)-(5.33) into (5.26) constitutes to the following equation:

$$N_{during\ process} = \frac{\left(\frac{Conc_{original} . w . h . U . \left\{ t_p + \left[\frac{(T/4) - t_p}{(T/4)} \right] . T \right\}}{m_p} \right) \cdot \left(\frac{L}{2.t_p . U} \right) \cdot \left(\frac{V_y}{V_x} \right)}{\frac{L.w}{4r^2}} \quad (5.34)$$

where L and w are the length and the width of the channel respectively.

When the numerical parameters under the experimental conditions shown in Fig 4.22 at concentration of 0.025 g/ml were inputted into equation (5.34), it was calculated that $N_{\text{during process}} > 13$. This meant that the channel was fully filled with particles under such conditions which was observed experimentally and rendered the equation reasonable for the prediction of particles in the channel.

Once equation (5.34) was conceived, Fig 4.22 was modified to relate $f(\text{conc})$ with that of $N_{\text{during process}}$ as shown in Fig 5.15. $f(\text{conc})$, at the individual $N_{\text{during process}}$ points, are the normalized values obtained by dividing the material removal rates at the different concentration in the slurry (as shown in Fig 4.22) with that of the maximum material removal rate corresponding to the optimum angle, $\hat{\alpha}_p$. As for $N_{\text{during process}}$, the points were calculated based on equation (5.34). The graph was then plotted with a best fitted polynomial curve (3rd order polynomial curve).

Fig 5.15 Relationship between $f(\text{conc})$ with that of $N_{\text{during process}}$ on gold (for 1.5 μm abrasive particles)

Fig 5.16 illustrates the procedural flowchart for the determination of the graph $f(conc)$ vs $N_{during\ process}$.

Fig 5.16 Procedural flowchart for the determination of the graph $f(conc)$ vs $N_{during\ process}$

5.2.2 Modelling process to determine material removal rate

In order to determine the material removal rate of the electrokinetic material removal process through calculation, Fig 5.15, equations (5.2) – (5.11) & (5.14) – (5.34) were utilized. The values of the C , n , K in the erosive models were calculated from the experimental results obtained from the experiments reported in Chapter 4 (i.e. Fig 4.14 – 4.18). The proposed model for the electrokinetic material removal process was used to

back-calculate all these values (based on the experimental results) before progressing onwards to calculate the rest of the MRRs for comparison with that of the experimented ones. Fig 5.17 shows the flowchart of the modelling process to determine the calculated MRR points.

Fig 5.17 Flowchart of the modelling process to calculate MRR

t_p was used based on the calculation from equation (5.11). t_p was based on the time taken for the particle to reach the surface of the workpiece from the centre of the channel (i.e. 0.5 H). However, t_p can be adjusted when $N_{during\ process}$ is too small or large, in order to obtain a more accurate calculated MRR as shown in Fig 5.17.

5.2.3 Results and discussion on the modelling of material removal rate

The results obtained from the modelling of material removal rate (MRR) are illustrated and compared with the measured experimental results.

The comparisons of the calculated and experimentally measured MRR are shown in Figs 5.18 – 5.21.

Fig 5.18 Graph showing the comparisons of calculated and experimentally measured values in MRR vs DC electric field strength graph for gold workpieces

Fig 5.19 Graph showing the comparisons of calculated and experimentally measured values in MRR vs AC electric field strength (pk-pk) graph for gold workpieces

Fig 5.20 Graph showing the comparisons of calculated and experimentally measured values in MRR vs AC electric field frequency graph for gold workpieces

Fig 5.21 Graph showing the comparisons of calculated and experimentally measured values in MRR vs fluid velocity graph for gold workpieces

According to Figs 5.18 – 5.21, maximum material removal rates occurred at certain parametric conditions. These maximum MRR points occurred largely due to the optimal concentration of the particles in the channel during the electrokinetic material removal process. Coincidentally, these maximum points arose at the optimal angle of impingement (for maximum material removal rate) which fell at approximately 20°.

It was observed that the calculated MRRs agreed reasonably well with the experimentally measured ones in general. Figs 5.18 – 5.21 showed that most of the calculated MRR points were within the range of experimentally measured values. This deemed the hypothesis that the electrokinetic material removal mechanism being analogous to that of the erosion material removal holds true. This also demonstrated that the modified erosion model is capable of relating the MRR for the electrokinetic material removal process to the parametric conditions.

To further validate this hypothesis, comparisons of the calculated and experimentally measured MRRs were performed on another workpiece material (i.e. aluminium). As the MRR model is based on the erosion material removal model which has a material related property embedded in it [112], it has certain relation to the hardness of the workpiece surface (relation embedded via C and p). The comparisons will be showed in the following chapter (Chapter 6).

5.3 Summary

The equation of motion based on Newton second law was modelled for the vertical trajectory of the abrasive particle. The equation was subsequently solved by using a numerical computing software (MATLAB[®]). The trajectories of the particle appeared to be similar to the predicted and observed motion of the abrasive particles during the experimentation. Modelling results showed that the velocities in the vertical direction of the particles were in the range of around 10 mm/s to 50 mm/s during the experimental processes that were carried out in Table 4.4

On the other hand, the horizontal velocity of the particle was modelled by using a multi-physics modelling software (COMSOL[®]). It was realized that the velocity of the particle when it is on the surface of the workpiece appeared to be about twenty percent of the general fluid velocity within the channel.

It appeared that the main material removal mechanism for the electrokinetic material removal process seemed to be a mechanically dominating one as the velocity of the particles far exceeded the minimum velocity to break the metallic gold bonds.

A model based on the erosion material removal was used to relate the MRR of the electrokinetic material removal process to the parametric conditions. The erosion model was previously used by other researchers [111] to reflect the material removal of emission elastic machining (EEM). Since the electrokinetic material removal process is similar to that of the EEM process, the erosion model was attempted to also describe our process. Slight modification was made to the erosion model by including a concentration function to it. The MRR was then calculated and compared to the experimentally measured ones. Results showed that the calculated and the experimentally measured MRR agreed reasonably. It also demonstrated that the modified erosion model is capable of relating the MRR for the electrokinetic material removal process to the parametric conditions.

Chapter 6

Application of electrokinetic material removal process on aluminium

This chapter consists of the results on material removal rate of the aluminium workpiece after it had undergone the electrokinetic material removal process. This chapter will work on another material besides gold to demonstrate the feasibility of the electrokinetic material removal process on metallic material. Aluminium material was eventually selected due to its vast application in the industry. This chapter will proceed on to study and compare the influences of the electrokinetic and hydrodynamic effects on the material removal rate (MRR) on aluminium material. A study of the material removal model as presented in chapter 5 will also be carried out to determine its validity for the aluminium material removal. An overview of the chapter is shown in Fig 6.1

Fig 6.1 Overview of Chapter 6

6.1 Electrokinetic material removal experiment on aluminium

The electrokinetic material removal process was proposed and determined in the previous chapters to be able to remove material in a non-contact manner. It was also proven to be feasible in removing material at the nanometric level mechanically which was analogous to that of erosion.

So far, only gold workpieces were used during the study of the electrokinetic material removal process where the material is costly and not widely used in manufacturing. Little work was performed on other more commonly used material to demonstrate the

feasibility of the method for material removal. Therefore, prior studies have to be made to other commonly used materials to further understand the material removal mechanism. These prior studies were performed to distinguish the differences in the material removal characteristics between the materials and to look into the feasibility of applying the electrokinetic material removal technique for industrial applications. Owing to the fact that aluminium is one of the most widely used materials and its versatility in the manufacturing industry, aluminium was ultimately selected for the study.

6.2 Experimental method

An identical setup to that as described in chapters 3 & 4 was intentionally constructed to study and compare the material removal characteristics between gold and aluminium material. The only difference, in the material removal experiments that is conducted in this chapter with that of the previous chapters, is that the sputtered material that was deposited onto workpiece was aluminium (pure aluminium sputtered wafer where the purity of the sputter target for the sputtering process is 99.999% pure aluminium (Kurt J. Lesker Company)) instead of gold. Fig 6.2 shows the schematic setup for the experiments that were carried out in this chapter.

Fig 6.2 Schematic setup

6.3 Results and discussion on the electrokinetic material removal of aluminium

This section will discuss on the results obtained from the experiments based on the material removal due to electrokinetic phenomenon. The section will be further divided into 2 subsections. Subsection 6.3.1 will discuss about the preliminary results on the electrokinetic material removal of the aluminium workpiece. The subsection will look mainly into the material removal mechanism on aluminium workpiece. This will be followed by subsection 6.3.2 where the influences of the electrokinetic and hydrodynamic effects on the electrokinetic material removal on aluminium material would be discussed. Consequently, section 6.3 will concluded with a comparison between the calculated MRR of the aluminium material with that of the experimental values in subsection 6.3.3. The comparison between the calculated and measured MRR is necessary as it validates the material removal model that was proposed in chapter 5.

6.3.1 Preliminary results and discussion on the electrokinetic material removal of aluminium

Preliminary results showed that it is possible to remove aluminium based on the electrokinetic material removal process. Fig 6.3 shows the material removal on the aluminium workpiece. With the results obtain in Fig 6.3, it has further revealed that the electrokinetic material removal process was capable of removing metallic material from the surface, besides gold only (as shown in the previous chapters), at the nanometric level.

Fig 6.3 Top view image of the material removed from an aluminium workpiece taken from the WYKO measurement system with a 2-D profile on the material removed from the workpiece in the X direction (direction along the channel located at the centre of the channel) and a 2-D profile on the material removed from the workpiece in the Y direction (direction perpendicular to the channel located at the centre of the channel)

Similar to the observation made in Fig 4.7, Fig 6.3 showed slightly greater material removal at the edge of the channel as compared to the centre. This may be attributed to the localized non-homogeneities of the electric field where the electric field was more concentrated at the edges due to the abrupt differences in the electrical resistivities of the PDMS and the ethanol as discussed previously (section 4.1.6).

To further understand the material removal mechanism of electrokinetic material removal process, studies were taken to determine the effects on the material removal of aluminium under the various conditions as previously shown in Fig 4.2. These studies were deliberately conducted under the same experimental conditions and presented in the same manner as that of Figs 5.8 & 5.9 to compare and distinguish the differences in the material removal characteristics for gold and aluminium materials. Fig 6.4 shows the effects of the material removal of aluminium over a period of 1 hour under the various conditions as shown previously in Fig 4.2. The raw measurements of the surface plots

were obtained by using the white light interferometer before a surface analysis software (Mountains[®] from Digital Surf) was utilized to post-process the data for comparisons.

Fig 6.4 The material removal on the aluminium workpiece when the abrasive particles in the slurry are under the influences of fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only (d) AC electric field with a DC bias (e) AC electric field with a DC bias (without abrasive particles). (Silicon oxide particle size: 1.5μm, particle concentration: 0.01g/ml, fluid velocity: 0.4 m/s, DC electric field strength: 12.5 kV/cm, AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

A quantification of the material removal due to the conditions (a)-(e) according to Fig 6.4 is shown in Fig 6.5.

Fig 6.5 Comparisons of the material removal on the aluminium workpiece when the abrasive particles in the slurry are under the influences of fluid flow and (a) no electric field (b) AC electric field only (c) DC electric field only (d) AC electric field with a DC bias (e) AC electric field with a DC bias (without abrasive particles). (Silicon oxide particle size: 1.5 μ m, particle concentration: 0.01g/ml, fluid velocity: 0.4 m/s, DC electric field strength: 12.5 kV/cm, AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

It was observed from Fig 6.5 that there was no material removal of aluminium when the particles were subjected to hydrodynamic effect only. Material removal on aluminium was observed only when the particles were subjected to both electrokinetic and hydrodynamic effects where substantial material removal in Fig 6.4 (b) & (c) and marked material removal in Fig 6.4 (d) were seen. Substantial material removal in Fig 6.4 (b) was expected as the particles were under the influence of fluid flow and AC electric field which embody the particles with sufficient velocity to achieve material removal on the

surface of the aluminum workpiece. Considerable material removal was seen in Fig 6.4 (c) where the material removal may be due to the frictional wear between the abrasive particles and surface of the workpiece. It was only when the particles were subjected to the influences of the fluid flow and the AC electric field with a DC bias that a marked material removal was recorded (shown in Fig 6.4 (d)). Experiment 6.4 (e) was undertaken to determine the electrochemical dissolution effect of the electrokinetic material removal to further validate that the dominant material removal was due to that of the mechanical mechanism as opposed to the electrochemical dissolution effect. As compared to the material removal rate (MRR) of gold as shown previously in Fig 5.9 (b) – (e), the MRR of aluminium in accordance to Fig 6.5 (b) – (e) appeared to be higher.

A comparison of the material removal between gold and aluminium workpiece was also made at varying time durations with the same conditions. This comparison is shown in Fig 6.6.

Fig 6.6 A comparison of the MRR on gold and aluminium workpieces when the abrasive particles in the slurry are under the influences of hydrodynamic and electrokinetic effects at different time durations. (Silicon oxide particle size: 1.5 μ m, particle concentration: 0.01g/ml, fluid velocity: 0.4 m/s, DC electric field strength: 12.5 kV/cm, AC electric field strength (pk-pk): 50.0 kV/cm and AC electric field frequency: 10 Hz)

It was observed that the material removal on both of the material were proportional to time duration. It was also observed that the material removal for the aluminium workpiece was higher than that of the gold workpiece at all times. The higher material removal for the aluminium workpiece could be due to the galvanic corrosion that was involved during the electrokinetic material removal process where an increase in the electrochemical dissolution was seen. The higher material removal on aluminium may also be due to the softer aluminium material [146] owing to the weaker metallic bonds within the material as compared to gold.

6.3.2 Results and discussion on the influences of the particle concentration, electrokinetic and hydrodynamic effects on the electrokinetic material removal of aluminium

This subsection will look into the influence of the particle concentration, electrokinetic and hydrodynamic effects on the electrokinetic material removal of aluminium. The comparison between the experimental data of the MRR of both gold and aluminium will be made and discussed in this subsection. Table 6.1 shows the experimental table for the studies that were carried out to look into the influence of each effect on the material removal of the process.

Table 6.1 Experimental table for electrokinetic material removal on aluminium

Experiment	Time	Particle type	Particle size	Concentration of particles	DC electric field strength	AC electric field strength (pk-pk)	AC electric field frequency	Fluid velocity
	(min)		(μm)	(g/ml)	(kV/cm)	(kV/cm)	(Hz)	(m/s)
Experiment 1 (Fig 6.7)	60	Silicon oxide	1.5	0.001 ~ 0.035	12.5	50	10	0.4
Experiment 2 (Fig 6.8)	60	Silicon oxide	1.5	0.01	0 ~ 25.0	50	10	0.4
Experiment 3 (Fig 6.9)	60	Silicon oxide	1.5	0.01	12.5	25 ~ 100	10	0.4
Experiment 4 (Fig 6.10)	60	Silicon oxide	1.5	0.01	12.5	50	5 ~ 500	0.4
Experiment 5 (Fig 6.11)	60	Silicon oxide	1.5	0.01	12.5	50	10	0.1 ~ 1.4

6.3.2.1 Results and discussion on the influence of the particle concentration effect on the electrokinetic material removal of aluminium with comparison to gold material

Fig 6.7 The influence of particle concentration effect on the MRR of gold and aluminium workpieces

The effect of the concentration of the particles on the MRR of gold was shown and discussed in the previous chapter. A similar set of experiment was performed on the aluminium workpieces to investigate the effect of the abrasive particle concentration and for comparison with the gold workpiece. Fig 6.7 shows the influence of abrasive particle concentration on the MRR of gold and aluminium. It was observed that the MRR on aluminium was higher than that of the gold material throughout all abrasive particle concentrations. This may be attributed to the weaker metallic bonds between the aluminium atoms and the galvanic corrosion of the aluminium as mentioned in the previous section.

When the concentration was extremely low (i.e. particle concentration ≤ 0.001 g/ml), the MRR of the workpieces were low. It was assumed that the MRR of the workpieces, at such low particle concentration, were mainly due to electrochemical dissolution effect. As the electrochemical dissolution of the aluminium is greater than that of gold, the MRR of aluminium was observed and expected to be higher at low abrasive particle concentrations. When the concentration of the abrasive particles rose, the MRR increased.

The increase in the MRR was due to the higher participation of the abrasive particles with the surface of the workpiece to cause mechanical material removal. The MRR for both the workpieces peaked at the same particle concentration which suggested that the channel was partially filled with particles for maximum MRR. When the particle concentration increased beyond 0.01 g/ml, the MRR decreased. This may possibly be due to the insufficient distance for the abrasive particles to gain velocity before colliding onto the surface of the workpiece to achieve material removal. Subsequently, it was observed that the MRR reached a low for both materials (particle concentration > 0.025 g/ml) as the channels for the slurry flow were fully packed with the abrasive particles. Interestingly, the difference in the MRR between the materials, beyond particle concentration of 0.025 g/ml, was greater than the difference in the MRR between the materials at extremely low concentration (particle concentration ≤ 0.001 g/ml). The difference in MRR (due to the electrochemical dissolution effect between the two materials) was supposed to be similar, or even larger, at extremely low particle concentration (particle concentration ≤ 0.001 g/ml) as compared to extremely high particle concentration (particle concentration > 0.025 g/ml). This is because the electrochemical dissolution effect may be hindered by the high concentration of particles (at extremely high particle concentration) as compared to extremely low particle concentration. This might lead to the differences in the MRR between the materials to be even smaller at extremely high particle concentration (particle concentration > 0.025 g/ml) than at extremely low particle concentration (particle concentration ≤ 0.001 g/ml). However, results showed otherwise. Therefore, the most likely reason for the greater difference in MRR (particle concentration > 0.025 g/ml) was due to the weaker metallic bonds between aluminum atoms within the softer aluminum workpiece.

6.3.2.2 Results and discussion on the influences of the electrokinetic and hydrodynamic effects on the electrokinetic material removal of aluminium with comparison to gold material

Figs 6.8-6.11 show the influences of the electrokinetic and hydrodynamic effects on the electrokinetic material removal of aluminium. The MRR graphs of the corresponding gold material were included in these graphs as comparisons. It was observed that the MRR for aluminium was higher than that of gold in all the graphs. The higher aluminium MRRs were attributed to the weaker aluminium bonds and higher material removal due to electrochemical dissolution. It was also observed that the MRR curves for both of the materials followed the same trend. The similarity in the MRR trend for both the material further verified the observations that were made earlier during the electrokinetic material removal of gold. In addition, it further confirmed that the electrokinetic process worked for all metallic material with similar material removal mechanism as demonstrated in earlier chapter. With the experiments on the material removal of aluminium workpieces carried out, the trend of the electrokinetic material removal shows strong similarity with that of the erosion material removal trend and mechanism. Since the concentration curve for both materials follow the same trend and the optimal angle of impingement for maximum material removal coincided at approximately the same angle [117], the MRRs for both materials peaked at roughly the same parametric conditions in all the graphs (i.e. Figs 6.8 – 6.11).

Fig 6.8 The influence of DC electric field strength on the MRR of gold and aluminium workpieces

Fig 6.9 The influence of AC electric field strength (pk-pk) on the MRR of gold and aluminium workpieces

Fig 6.10 The influence of AC electric field frequency on the MRR of gold and aluminium workpieces

Fig 6.11 The influence of fluid velocity on the MRR of gold and aluminium workpieces

6.3.3 Results and discussion on the modelling of material removal rate for aluminium

An attempt on the modelling of the MRR for aluminium was made. The modelling process was based on the flowchart as shown previously in Fig 5.16. Since the MRR model was a semi-empirical one that relied on the MRR vs concentration curve, a similar set of experiment was performed on the aluminium material to retrieve the MRR vs concentration curve for aluminium. The MRR vs concentration curve for aluminium was shown earlier on in Fig 6.7. However, the graph had to be modified to relate $f(\text{conc})$ with that of $N_{\text{during process}}$ as shown in Fig 6.12 (refer to Fig 5.16 for the procedural flowchart to determine the graph $f(\text{conc})$ vs $N_{\text{during process}}$). The graph was then plotted with a best fitted polynomial curve (3rd order polynomial curve) before the MRR was calculated. Fig 6.13 shows the flowchart of the modelling process that was used to calculate the MRR for the aluminium material.

Fig 6.12 Relationship between $f(\text{conc})$ with that of $N_{\text{during process}}$ on aluminium (for 1.5 μm abrasive particles)

Fig 6.13 Flowchart of the modelling process to calculate MRR for aluminium

The results obtained from the modelling of MRR of the aluminium material were compared with the measured experimental values.

The comparisons of the calculated and experimentally determined MRRs are shown in Figs 6.14 – 6.17.

Fig 6.14 Graph showing the comparisons of calculated and experimentally measured values in MRR vs DC electric field strength graph for aluminium workpieces

Fig 6.15 Graph showing the comparisons of calculated and experimentally measured values in MRR vs AC electric field strength (pk-pk) graph for aluminium workpieces

Fig 6.16 Graph showing the comparisons of calculated and experimentally measured values in MRR vs AC electric field frequency graph for aluminium workpieces

Fig 6.17 Graph showing the comparisons of calculated and experimentally measured values in MRR vs fluid velocity graph for aluminium workpieces

It was observed that the calculated MRRs agreed reasonably within the range of the experimentally measured MRRs for the aluminum workpieces. According to Figs 6.14 – 6.17, the maximum MRRs generally occurred at the optimal concentration and frequently arose at the optimal angle of impingement (for maximum material removal rate) which fell at about 20° . The same trend was also previously observed for the gold material in chapter 5.

Since the MRR model agreed relatively well to the measured MRRs, it could be concluded that the mechanical material removal mechanism of the electrokinetic material removal process was similar to that of the erosion process. The results obtained from Figs 6.14 – 6.17 had further demonstrated that the modified erosion model was capable of relating the MRR for the electrokinetic material removal process to the parametric conditions.

6.4 Summary

The electrokinetic material removal process was carried out on the aluminium workpieces to demonstrate the feasibility of removing material by using this technique on other metallic material. The main objectives for the experiments for this chapter are listed as follow:

- To apply the electrokinetic material removal process for industrial applications by removing material on aluminium where the material is widely used in the manufacturing industry
- To distinguish the similarities and differences in the material removal characteristics between gold and aluminium material
- To confirm that the material removal mechanism of the electrokinetic material removal process was analogous to the erosion process
- To verify that the modified MRR model that was proposed in chapter 5 was capable in relating the MRR for the electrokinetic material removal process to the parametric conditions

Experiments were subsequently intentionally carried out for these purposes of studies.

Preliminary results showed that the electrokinetic material removal process was capable of removing material from the surface of the workpieces in a non-contact manner at the nanometric level. The mechanism of the material removal of the aluminium workpieces in the electrokinetic material removal process was subsequently determined and compared with that of the gold workpieces. Results showed that the MRRs were higher for the aluminium workpieces as compared to the gold ones. The higher aluminium MRRs were attributed to the weaker aluminium bonds between the atoms and higher material removal due to electrochemical dissolution.

The influences of the electrokinetic and hydrodynamic effects on the material removal rates of the process were subsequently studied. The material removal rates of the electrokinetic material removal process on aluminium workpieces were determined to be within a range of about 700 Angstrom/Hr to 3200 Angstrom/Hr.

It was realized that the MRR curves for the material removal on both material followed the same trend which was analogous to the erosion material removal process. An attempt to prove that the modified erosion model (proposed in chapter 5) was capable in determining the MRRs of the material removal process was made. Results showed that the calculated MRRs of the aluminium based on the modified erosion model were in reasonable agreement with that of the measured ones.

Thus, this chapter has further demonstrated that the electrokinetic material removal process is capable in removing material on metallic surfaces. The chapter has also covered the material removal mechanism and parametric studies of the process for the aluminium material. The results have shown that the material removal mechanism is analogous to that of the erosion process. It has also further demonstrated that the modified erosion model is capable of relating the MRR for the electrokinetic material removal process to the parametric conditions.

Chapter 7

Investigation on surface roughness after electrokinetic material removal process

This chapter covers the results on the surface roughness of the workpieces after the electrokinetic material removal process. The chapter looks into the surface roughness of the gold and aluminium workpieces after the electrokinetic material removal process. The chapter will demonstrate the influences of the electrokinetic and hydrodynamic effects of the process on the surface finish of the workpieces, with attempts made to explain these effects on the surface roughness after the process. The first part of the chapter will provide an insight on the influences of the electrokinetic and hydrodynamic effects on the surface finish while the second part of the chapter will subsequently investigate the performance of using the electrokinetic material removal process for the improvement of the surface quality of the workpiece.

Fig 7.1 Overview of Chapter 7

7.1 Electrokinetic material removal experimental study of surface roughness of workpieces

The electrokinetic material removal process was shown in the previous chapters to be capable of achieving nanometric material removal. The main advantage of using the electrokinetic material removal process is that, apart from the particles, there is no physical contact with the workpiece to induce possible defects on it. Although the material removal of the workpieces can be controlled with high precision, studies on the surface roughness generated from the process are necessary to look into the surface quality of the workpieces.

While the previous chapters emphasized on the material removal rates (MRRs) of workpieces, this chapter will elaborate on the surface finish of the workpieces after the material removal process. The first part of the chapter will look into the influences of the electrokinetic and hydrodynamic effects on the surface finish of the workpiece after the material removal process by conducting on extremely smooth workpieces. The later part of the chapter will then be conducted on predetermined rough workpiece surfaces to investigate the performance of the electrokinetic material removal process for the enhancement of the surface quality of the workpieces.

It is through these studies that a better understanding of how the process can be controlled and optimized; to precisely remove material while generating a finished surface with predetermined roughness.

7.2 Experimental method for the study of surface roughness of workpieces

The experimental setup for the surface roughness study was constructed in accordance to the one shown in earlier chapters (i.e. Figs 3.2 and 6.2). Instead of determining the material removal on the workpieces over the span of time (previously reported in chapters 4 and 6), surface roughness measurements were made to understand the

relationship between the surface roughness of the workpieces with respect to the influencing parameters in this chapter. The surface roughness of the workpiece was determined by using atomic force microscopy (AFM) where it was reported to be one of the most accurate measurement systems available for the determination of surface roughness at the nanometric level [130]. During the evaluation of the surface roughness on the workpieces, the root mean squared roughness, RMS, was used instead of the arithmetic average roughness, Ra. This is because RMS can be used to interpret fine surfaces in scientific measurements with statistical evaluations. As RMS represents the standard deviation of the profile height distribution, it is more sensitive to peaks and valleys, and hence statistically more meaningful as compared to Ra.

As mentioned in the previous section, the surface roughness study will be divided into two parts: i) surface roughness study on extremely smooth surfaces (~ 2 nm RMS for gold workpieces and ~ 5 nm RMS for aluminium workpieces) and ii) surface roughness study on workpieces with predetermined rougher surfaces (~ 80 nm RMS for gold workpieces and ~ 90 nm RMS aluminium workpieces). Table 7.1 shows the range of process parameters used in the experiments for the following sections.

For the surface roughness results in the following section, the measurements were taken after the workpieces had undergone 1 hour of the electrokinetic material removal process. A total of 10 measurements (across the channel) were taken for each data point. The sample mean and standard deviation of the surface roughness was then calculated and plotted on each graph.

Table 7.1 Experimental table for surface roughness study after the electrokinetic material removal process

Experiment	Particle type	Particle size	Concentration of particles	Time	DC electric field strength	AC electric field strength (pk-pk)	AC electric field frequency	Fluid velocity
		(μm)	(g/ml)	(min)	(kV/cm)	(kV/cm)	(Hz)	(m/s)
Experiment 1 (Fig 7.3)	Silicon oxide	1.5	0.01	15 ~ 75	12.5	50	10	0.4
Experiment 2 (Fig 7.4)	Silicon oxide	1.5	0.01	60	0 ~ 25.0	50	10	0.4
Experiment 3 (Fig 7.5)	Silicon oxide	1.5	0.01	60	12.5	25 ~ 100	10	0.4
Experiment 4 (Fig 7.6)	Silicon oxide	1.5	0.01	60	12.5	50	5 ~ 500	0.4
Experiment 5 (Fig 7.7)	Silicon oxide	1.5	0.01	60	12.5	50	10	0.1 ~ 1.4
Experiment 6 (Fig 7.8)	Silicon oxide	1.5	0.01	60	0 ~ 25.0	50	10	0.4
Experiment 7 (Fig 7.9)	Silicon oxide	1.5	0.01	60	12.5	25 ~ 100	10	0.4
Experiment 8 (Fig 7.10)	Silicon oxide	1.5	0.01	60	12.5	50	5 ~ 500	0.4
Experiment 9 (Fig 7.11)	Silicon oxide	1.5	0.01	60	12.5	50	10	0.1 ~ 1.4
Experiment 10 (Fig 7.15)	Silicon oxide	1.5	0.01	15 ~ 60	12.5	50	10	0.4
Experiment 11 (Fig 7.16)	Silicon oxide	1.5	0.01	60	0 ~ 25.0	50	10	0.4
Experiment 12 (Fig 7.17)	Silicon oxide	1.5	0.01	60	12.5	25 ~ 100	10	0.4
Experiment 13 (Fig 7.18)	Silicon oxide	1.5	0.01	60	12.5	50	5 ~ 500	0.4
Experiment 14 (Fig 7.19)	Silicon oxide	1.5	0.01	60	12.5	50	10	0.1 ~ 1.4

7.3 Results and discussion on the study of surface roughness

Workpieces of two different range of surface roughness were used for the experiment: i) smooth surfaces and ii) rougher surfaces. The intention of carrying out the two sets of experiment was to look into the parametric effects on surfaces finish and the surface enhancement after the electrokinetic material removal process respectively.

7.3.1 Results and discussion on the study of surface roughness on smooth surfaces

For workpieces of smooth surfaces, the silicon wafers were prepared by oxidizing a layer of silicon dioxide onto the surface of the wafer before subsequently sputtering it with 500 nm of the metallic film. The study on the surface roughness was performed on both the gold and aluminium workpieces. These surface roughness curves were subsequently plotted onto the same graph for comparison.

Fig 7.2 shows the surface roughness scans that were obtained before and after the electrokinetic material removal process respectively for both the gold and the aluminium material. It was observed that the surface roughness on the workpieces obtained after the electrokinetic material removal were higher than that of the original smooth surfaces.

Fig 7.2 Surface topography of the gold ((a) & (b)) and aluminium ((c) & (d)) workpieces obtained from the AFM (Silicon oxide particle size: 1.5 μ m, particle concentration: 0.01g/ml, fluid velocity: 0.4 m/s, DC electric field strength: 12.5 kV/cm, AC electric field strength (pk-pk): 80.0 kV/cm and AC electric field frequency: 10 Hz)

Fig 7.3 shows the surface roughness of the gold and aluminium workpieces after undergoing the process over a range of durations. It was observed that the surface roughness obtained on aluminium was higher than that of the gold material which may be attributed to the softer material properties of the aluminium material. The softer material property of the aluminium material led to higher material removal (Fig 6.6) and higher surface roughness on the workpiece as more material were transferred/removed from the surface as compared to gold. This led to more layers of atoms removed from the surface which incurred more material removal and higher surface roughness.

It was also observed from Fig 7.3 that there is a relationship between the surface roughness and time. However, after approximately 45 minutes, the rate of increase in the surface roughness appeared to level out. It was suggested that the surface roughness of the workpiece during the material removal process reached a plateau after approximately 45 minutes of the electrokinetic material removal process.

Fig 7.3 Surface roughness of the gold and aluminium workpieces (smooth) at different time intervals

Subsequently, parametric studies were carried out to investigate the influences of the electrokinetic and hydrodynamic effects on the surface finish of the process. Figs 7.4 -7.7 show these results.

Fig 7.4 The influence of DC electric field strength on the surface finish of the gold and aluminium workpieces (smooth)

Fig 7.5 The influence of AC electric field strength (pk-pk) on the surface finish of the gold and aluminium workpieces (smooth)

Fig 7.6 The influence of AC electric field frequency on the surface finish of the gold and aluminium workpieces (smooth)

Fig 7.7 The influence of fluid velocity on the surface finish of the gold and aluminium workpieces (smooth)

From Figs 7.4-7.7, it was observed that the influences of the experimental parameters on the surface roughness on both the gold and aluminium workpieces after the material removal process followed the same trend where they peaked at the same parametric conditions. Furthermore, it was also observed that the surface roughness curves were analogous to the material removal rate (MRR) curves that were reported in the earlier chapters.

As a comparison between the surface roughness curves and the MRR curves influenced by the experimental parameters, both of the curves were plotted together in the same graph as shown in Figs 7.8 – 7.11. Figs 7.8 – 7.11 show the graphs of the surface roughness and MRR curves that were plotted together for comparison purposes on the gold material.

Fig 7.8 The influence of DC electric field strength on the surface roughness and the material removal rate of the gold workpieces (smooth)

Fig 7.9 The influence of AC electric field strength (pk-pk) on the surface roughness and the material removal rate of the gold workpieces (smooth)

Fig 7.10 The influence of AC electric field frequency on the surface roughness and the material removal rate of the gold workpieces (smooth)

Fig 7.11 The influence of fluid velocity on the surface roughness and the material removal rate of the gold workpieces (smooth)

Figs 7.8 – 7.11 show the influences of the experimental parameters on the surface roughness and the material removal rate of the gold workpiece. It was observed that the surface roughness and the material removal rate increased when the influencing parameters incremented towards the optimal condition for maximum MRR. The rise in the surface roughness and the MRR was due to the increase in abrasive particles interacting with the surface of the workpiece for material removal. Furthermore, by incrementing the influencing parameters, it also raised the particles' velocity and angle of impingement which led to greater material removal and hence a rougher surface. However, when the influencing parameters were increased beyond the optimal condition for maximum MRR, both the surface roughness and MRR began to decrease. The decrease in MRR was expected (as explained in chapter 4) but the decrease in the surface roughness was not. This is because the surface roughness of the workpieces were expected to increase further in the case of the erosion material removal process [159]. A possible explanation for the decrease in the surface roughness in Fig 7.8 is due to the magnitude of velocity that was utilized during the electrokinetic material removal process. As compared to the conventional erosion process [104,159,160], the velocities of the abrasive particles, in the electrokinetic material removal process, were much smaller than that of the reported ones. The further increase in the surface roughness of the workpieces after the material removal process with higher particle velocities and angles

of impingement in the reported work (erosion process) were attributed to the wear deformation mechanism [159] where the velocities of the abrasive particles were more than a hundred times faster than the electrokinetic material removal process. In contrary, the velocities in the electrokinetic material removal process were only a few times higher than the minimum velocity required to break the metallic bonds of the material for removal. Therefore, material removal relied heavily on the interactions, velocities and angle of impingements of the abrasive particles. When more material is removed from the surface, more layers of atoms are removed from it. As the velocities of the particles are a few times higher than that of the minimum velocity for atomic removal, the atoms of the workpieces are removed in small amounts (such as clusters) at a time which resulted in different roughness on the surface at various influencing parameters. As a result, it appeared that the surface roughness was influenced by and proportional to the MRR of the workpiece during the electrokinetic material removal process. The relationship between the surface roughness and the MRR for both the gold and aluminium workpieces is shown in Fig 7.12 where the surface roughness of the workpiece was plotted against the MRR. The graph was then plotted with best fitted polynomial curves (2nd order polynomial curves). It was observed that the surface roughness of the workpiece increased with higher MRR.

Fig 7.12 A graph showing the relationship between surface roughness and the material removal rate of the gold and aluminium workpieces (smooth)

7.3.2 Results and discussion on the study of surface roughness on rough surfaces

It appeared that the surface produced by the electrokinetic material removal process was at best limited to a roughness of approximately 2 nm RMS and 5 nm RMS for the gold and aluminium workpieces respectively from section 7.3.1. However, it would be more interesting to remove the material from an initial rougher surface and enhance the surface quality of the workpiece to a smoother surface.

In this study, the workpieces were roughened to obtain a predetermined rougher surface. The silicon wafers were prepared by undergoing a deep ion reactive etching (DRIE) process in order to obtain a predetermined rougher surface. Subsequently, the wafers were sputtered with a metallic film. In the study, surface roughness of predetermined rougher gold and aluminium workpieces were both investigated after the electrokinetic material removal process.

During the surface roughness study of predetermined rougher workpieces, studies were made in achieving a suitable predetermined surface as a platform for the experiments before the electrokinetic material removal processes were proceeded. Metallic surfaces with initial surface roughness in different ranges were tested. Table 7.2 shows the various initial surfaces tested and the surface roughness of the workpiece after it underwent the electrokinetic material removal process.

Table 7.2 Comparison study of surface roughness on rough workpieces before and after the electrokinetic material removal process

Workpiece	Material	Initial surface roughness before material removal process	Surface roughness after material removal process	Reduction in surface roughness
		RMS (nm)	RMS (nm)	(%)
a	Gold	11	11	~ 0
b	Gold	30	31	~ 0
c	Gold	75	50	~ 33
d	Aluminium	36	36	~ 0
e	Aluminium	85	59	~30

It appeared that gold workpieces *c* and aluminium workpiece *e* demonstrated a reduction in the surface roughness after the electrokinetic material removal process. It was observed that the other samples with lower initial predetermined surface roughness values did not experience discernable enhancement in terms of surface quality. A possible reason was that these surfaces were too smooth to start with to notice a considerable improvement in the surface roughness. Therefore, gold workpieces with initial predetermined surface roughness similar to gold workpiece *c* and aluminium workpiece *e* were used for the subsequent experiments to study the influencing parametric effects on the enhancement of surface finish on the gold and aluminium workpieces. The AFM images of the gold workpiece *c* and aluminium workpiece *e* before and after the electrokinetic material removal process are shown in Fig 7.13 and 7.14 respectively.

Fig 7.13 The enhancement of the surface finish on workpiece *c* after the electrokinetic material removal process (a) before process (b) after process

Fig 7.14 The enhancement of the surface finish on workpiece *e* after the electrokinetic material removal process (a) before process (b) after process

Fig 7.15 shows the surface roughness of the gold and aluminium workpieces at different time intervals after the electrokinetic material removal process. It seemed that the surface roughness of the rough workpieces decreased with increasing time duration of the material removal process. Similarly to Fig 7.3, the decrease in the surface roughness of the material appeared to be rather mild after approximately 45 minutes of the material removal process. Subsequently, parametric studies were carried out to investigate the influences of the electrokinetic and hydrodynamic effects on the enhancement of the surface roughness on the rough workpieces.

Fig 7.15 Surface roughness of the gold and aluminium workpieces at different time intervals

Figs 7.16 – 7.19 show the influencing parametric effects on the surface enhancement on the gold and aluminium workpieces. As a comparison, the surface roughness curves for the smooth workpieces that were previously reported in section 7.3.1 were plotted within the same graph against the influencing parameters of the electrokinetic material removal process.

Fig 7.16 The influence of DC electric field strength on the surface finish of the gold and aluminium workpieces

Fig 7.17 The influence of AC electric field strength (pk-pk) on the surface finish of the gold and aluminium workpieces

Fig 7.18 The influence of AC electric field frequency on the surface finish of the gold and aluminium workpieces

Fig 7.19 The influence of fluid velocity on the surface finish of the gold and aluminium workpieces

It was observed from Figs 7.16 – 7.19 that the surface roughness for the rough workpieces decreased with increasing influencing parameters until the optimal condition for maximum MRR was met. However, when the influencing parameters rose beyond the optimal condition for maximum MRR, the surface roughness started to increase. It appeared from the graphs that the surface roughness of the rough workpieces were to a certain extent in a reciprocal relationship to the surface roughness of the smooth workpieces. This relationship may be due to the MRR of the workpiece during the material removal process. The MRR of the rough workpieces were investigated and were found to be similar to the smooth workpieces. This showed that the MRR was not affected by the surface roughness of the workpieces.

The reduction in the surface roughness with higher influencing parameters (until the optimal condition for maximum MRR was met) was due to the increase in the MRR of the workpieces. When the MRR increased, it was suggested that more material on the peaks of the surfaces were removed which was evident in Fig 7.13 and 7.14. The material removal of the peaks led to a decrease in surface roughness and hence a smoother surface.

When the influencing parameters increased beyond the optimal condition for maximum MRR, MRR decreased. This constituted to the fact that lesser material were removed from the peaks to obtain a smoother surface and led to a rise in the surface roughness with increasing influencing parameters. However, this trend did not appear to be the case for the rough workpieces in Fig 7.17 and 7.19. It was suggested that the workpieces did not experience an increase in the surface roughness with further increment in the influencing parameters (beyond the parametric conditions for maximum MRR) as these parameters were previously shown to be able to achieve considerably higher MRR with yet a low surface roughness (on smooth workpieces). The ability of producing high MRR with yet a low surface roughness were believed to be attributed mainly to the angle of impingement and velocities of the abrasive particles during their cyclic collisions with the workpieces.

As the electrokinetic material removal process had demonstrated that it could achieve material removal down to a surface roughness of less than 20 nm RMS, it is possible that the process has the potential to reduce the rough surface of the workpieces to a surface roughness around that figure when, perhaps, undergoing a longer material removal time.

The surface roughness of the rough workpiece after the electrokinetic material removal process was measured to be as low as 35 nm RMS and 60 nm RMS for the rough gold and aluminium workpieces respectively. The results constituted to a reduction of approximately 50% of its original surface roughness (75nm RMS) for the rough gold material and a reduction of approximately 30% of its original surface roughness (85nm RMS) for the rough aluminium material.

7.4 Summary

The study of the surface roughness of the workpieces was performed in this chapter. The study was undertaken on the gold and the aluminium workpieces. The surface roughness study was broken into 2 parts. The first part was carried out on the smooth workpieces to investigate the influences of the electrokinetic and the hydrodynamic effects on the surface finish of the workpieces. Conversely, the second part of the study was performed on initial predetermined rough surfaces to look into the surface enhancement of the workpieces after the electrokinetic material removal process.

The first part of the study showed that the surfaces of the smooth workpieces were not enhanced where the surface roughness of the workpieces after the material removal process were in the range of 2 – 20 nm RMS. During the first part of the study, it was observed that the surface roughness of the workpieces after the material removal process were proportional to the material removal rate. It was suggested that the surface roughness increased with higher MRR as the atoms of the workpieces were removed in greater amounts at a time resulting to a rougher surface.

In the second part of the study, the surfaces of the predetermined rough workpieces were enhanced where a reduction in the surface roughness was observed. The surface roughness of the rough workpieces after the electrokinetic material removal process were measured to be as low as 35 nm RMS which constituted to a reduction of approximately 50% of its original surface roughness (gold material).

It is through the material removal rate and surface roughness studies that a better understanding can be obtained to control and possibly optimize the electrokinetic material removal process. In this way, it allows one to precisely remove the material while generating a finished surface with a predetermined surface roughness.

Chapter 8

Conclusions and future work

This chapter presents the concluding remarks pertaining to the electrokinetic material removal process. The key findings in the report will be highlighted and summarized. In addition, potential research tracks will be presented to further understand and improve the process as future work. An overview of the chapter is shown in Fig 8.1

Fig 8.1 Overview of Chapter 8

8.1 Conclusions

Miniaturization of devices has become one of the crucial engineering criteria to reduce cost, increase device performance and improve aesthetic appearance of the products. The miniaturization of the devices involves fabrication technologies that include addition and removal of material in the micrometric and even nanometric level. As such, material removal at the nanometric level has garnered a large interest and has posed a great challenge to satisfy the global market demand in producing ever smaller devices with higher dimensional accuracy and functional capabilities. Free abrasive machining is one of the technologies that is able to meet these demands without incurring unwarranted defects on the surface of the product.

The literature review showed a variety of free abrasive techniques where the non-contact polishing ones (where the machining tool is not in contact with the workpiece [1-4]) appeared to be the most attractive as the absence of the polishing pads minimize the presence of defects in conventional polishing such as microscratches. In order to achieve atomic-size machining, float polishing and elastic emission machining (EEM) were introduced to achieve extremely smooth surfaces with atomic machining accuracy. However, these techniques usually require a stringent precision movement control of the polishing tool (in the case of float polishing and rotating tool type EEM) or are hindered by the extremely slow material removal rate (nozzle type EEM). Therefore, non-contact material removal concepts were investigated in order to achieve atomic-size machining generating extremely smooth surfaces with atomic machining accuracy. Material removal utilizing electrokinetic phenomenon (a.k.a electrokinetic material removal process) was proposed as a non-contact process to achieve a smooth surface with minimal damages and strain. The proposed technique utilized the electrokinetic and hydrodynamic effects to manipulate the trajectories of the abrasive particles to achieve material removal on the workpiece. During the material removal study, a combination of DC and AC electric fields was proposed. To study the technique further, fabrication methods of the channels and the selection of the materials were made to look at the mechanical aspect of the material removal process. The experimental setup and procedure during the material removal process was presented.

Initial results showed a noticeable material removal on the workpiece and demonstrated the feasibility of the process for material removal from the surface of the workpiece. Results showed that the technique was feasible in achieving a smooth surface through nanometric material removal. Experiments were designed to study some of the effects of the various parameters that could affect the material removal rate (MRR) on the surface of the workpiece. The effects of the parameters were subsequently presented and discussed.

Modelling of the trajectory of the abrasive particles during the material removal process was undertaken. Modelling results based on the resultant velocities of the abrasive particles suggested that the velocities of the particles were much higher than the minimum velocity that is necessary to break the metallic bonding of the metallic atoms. This consequently led us to suggest that the mechanical mechanism to be a likely method for the material removal on the workpiece. Other material removal mechanisms were regarded as insignificant as there were insufficient evidence to suggest their presence.

Identification of the possible mechanical material removal mechanisms that were associated with the proposed process was made where the material removal process appeared to be analogous to that of the erosion process. A material removal model for the electrokinetic material removal process was subsequently proposed, based on a modification of the erosion model. Comparisons between the calculated and experimentally measured MRRs were made where the values agreed reasonably.

The electrokinetic material removal was performed on a more commercially viable material (i.e. aluminium). Results showed that the electrokinetic material removal process was capable of removing material from the aluminium surfaces. The electrokinetic material removal on aluminium workpieces were compared with the gold workpieces and results showed that the MRR for aluminium was higher than that of the gold. The higher aluminium MRRs were attributed to the weaker aluminium bonds between the atoms and the higher material removal due to electrochemical dissolution. An attempt to prove the

capability of the proposed electrokinetic material removal model was made on aluminium material and results further showed that both the experimentally measured and the calculated values were in reasonable agreement.

In order to study the surface conditions of the workpieces after the electrokinetic material removal process, a study on the surface roughness of the workpieces was performed. The study looked into the electrokinetic and hydrodynamic effects on the surface condition of the workpieces after the material removal process. Results showed corresponding trend with respect to the parametric effects on MRRs. The surface roughness results also showcased the ability to enhance the surface quality of the workpieces after the electrokinetic material removal process. The surface roughness of the rough workpieces was measured to be as low as 35 nm RMS which constituted to a reduction of approximately 50% of its original surface roughness (gold material).

It is through the material removal rate and the surface roughness studies that a better understanding can be obtained to control and possibly optimize the electrokinetic material removal process. In this way, it allows one to precisely remove the material while generating a finished surface with a predetermined surface roughness.

Table 8.1 shows the comparison of the electrokinetic material removal process vis-à-vis the state of art.

Table 8.1 Comparisons of the state of art machining techniques with that of the electrokinetic material removal process

Machining technique	Advantages	Limitations
Conventional polishing	<ul style="list-style-type: none"> • Able to produce planarized and flat surfaces 	<ul style="list-style-type: none"> • Contact process • Machining load from the polishing pad causes defects such as microscratches
Float polishing	<ul style="list-style-type: none"> • Non-contact process • Able to produce planarized and flat surfaces • Atomic material removal process • Chemical used is non-toxic 	<ul style="list-style-type: none"> • Requires the workpiece surface to be smooth before machining [1] • Requires a high precision technology to mount the polishing tool at a particular distance from the workpiece • Rotating tool has to rotate above a certain speed to achieve the non-contact polishing condition [64]
Elastic emission machining (Rotating tool type)	<ul style="list-style-type: none"> • Non-contact process • Atomic material removal process • Chemical used is non-toxic 	<ul style="list-style-type: none"> • Requires a high precision technology to mount the rotating tool during material removal process [3] • Rotating tool has to rotate above a certain speed to achieve the non-contact polishing condition [66]
Elastic emission machining (Nozzle-head type)	<ul style="list-style-type: none"> • Non-contact process • Atomic material removal process • Chemical used is non-toxic 	<ul style="list-style-type: none"> • Requires a high precision technology to mount the workpiece during material removal process [82] • A very slow process [42] (as slow as 1nm/Hr)
Magnetic field assisted finishing	<ul style="list-style-type: none"> • Non-contact process • Chemical used is usually non-toxic 	<ul style="list-style-type: none"> • The surface finish is usually in the range of around 50nm to 100nm Ra [46,58]
Electric field assisted finishing	<ul style="list-style-type: none"> • Non-contact process • Quality surface finish between 1nm Ra and 10nm Ry has been achieved in electrolytic abrasive finishing [79] 	<ul style="list-style-type: none"> • Utilizes chemical reaction for material removal • Chemical used is rather toxic
Electric and magnetic field assisted finishing	<ul style="list-style-type: none"> • Non-contact process • Quality surface finish of Ra 20nm has been achieved in electrolytic magnetic abrasive finishing [73] 	<ul style="list-style-type: none"> • Utilizes chemical reaction for material removal • Chemical used is rather toxic
Electrokinetic material removal process	<ul style="list-style-type: none"> • Non-contact process • Quality surface finish of RMS 2nm has been achieved in electrokinetic material removal process • Ability to create material removal in the nanometric order • Chemical used is non-toxic. 	<ul style="list-style-type: none"> • A slow process with MRR of approximately 200nm/Hr • However, as compared to nozzle-head type elastic emission machining, it is still much faster.

8.2 Major contributions

The major contributions of the accomplished work are listed below:

- A novel non-contact material removal method utilizing electrokinetic phenomenon was introduced. As the proposed process is a non-contact one, surface defects that may possibly be introduced onto the surface of the workpiece are minimized
- For the very first time, the feasibility of using the electrokinetic phenomenon to impinge the abrasive particles onto the surface of the workpiece for material removal was demonstrated. Results showed that the electrokinetic material removal process was capable of achieving nanometric material removal while generating a smooth surface as low as 2 nm RMS.
- The parametric influences of the electrokinetic and hydrodynamic effects on the material removal rate for both gold and aluminium workpieces were made to further study and understand the material removal process. Identification of the material removal mechanism was carried out before a semi-empirical model was proposed to relate the material removal rate with the influencing parameters on the novel electrokinetic material removal process.
- Consequently, parametric studies were carried out to look into the surface finish that the process could achieve. Results showed that the proposed process is promising in achieving nanometric material removal while generating a smooth finish on the workpieces.

8.3 Future work

The current work reported thus far has showcased the concept, feasibility and capability of the electrokinetic material removal process. However, further work can be performed to better understand and improve the process. These work are selected based on the information gathered from available literature and the results reported in this thesis. Key areas identified for further investigation are:

1. Utilizing slurry with better material properties for the slurry
2. Utilizing magnetic field to manipulate the trajectory of the abrasive particles instead of using electric field
3. Consideration of turbulent conditions in the study of electrokinetic material removal process
4. Integration of electrokinetic material removal technique on existing material removal process

The first and second areas are suggested because of the limitation of the abrasive particles' velocities due to the electrokinetic effect while the third area is suggested to further apply the concept on existing processes to enhance the surface finish of the products after the hybrid material removal process.

8.3.1 Utilizing slurry with better material properties

As mentioned in Chapter 4, the fluid for the slurry was based on the higher dielectric strength. The dielectric fluid has to be of higher dielectric strength due to the following reasons:

- To allow particle impingement at higher velocity by allowing a higher electric field strength to be supplied to the electrodes before dielectric breakdown occurs
- To prevent excessive electrochemical dissolution
- To prevent dielectric breakdown for electrical discharge from taking place
- To prevent the build up of temperature to allow boiling to happen

On top of that, some of the other properties of the fluid that are important for a higher material removal rate (MRR) during the process are the high dielectric constant (for higher electrokinetic effect) and low viscosity (for lower drag force) based on equations (5.8) and (5.11) respectively.

Ethanol was used as the fluid as it was environmentally benign. However, when the MRR of the process is of priority concern, other fluids with better properties can be investigated also.

During the study, silicon oxide abrasive particles were mainly used. A comparison was also made by utilizing the aluminium oxide abrasive particles. It was realized that sharp particles with high zeta potential were desired.

If a good selection of the abrasives and fluid were made, the electrokinetic material removal process may be further enhanced.

8.3.2 Utilizing magnetic field to manipulate the trajectory of the abrasive particles instead of using electric field

A limitation on the electrokinetic effect to manipulate the trajectories of the abrasive particles for the removal of material from the workpieces were observed and reported. In order to provide a wider range of material removal for the workpiece, magnetic field can be used where magnetic field may exhibit larger effects than the electric field [73,81]. Also, when the magnetic field is used to manipulate the trajectories of the abrasive particles, the MRR of the process may no longer be limited to the material properties of the slurry as reported in section 8.3.1. Furthermore, by using the magnetic field, the range of workpieces that can be used for the process is not limited to metallic materials only, but rather, a wider range of other materials (such as brittle material).

8.3.3 Consideration of turbulent conditions in the study of electrokinetic material removal process

It has been reported that turbulent conditions will increase the impact velocity of the abrasive particles, number of collisions per unit time and accelerate material removal rate in typical free abrasive machining processes [104]. However, turbulent conditions were not experimented during the electrokinetic material removal process. This is because the emphasis of the thesis was to study the influence of the electrokinetic phenomenon on the material removal rate of the proposed process where efforts were made during the study in the thesis to clearly understand the influence of both the hydrodynamic and electrokinetic effects on the material removal rate. As such, an empirical model was able to be successfully proposed to predict the material removal rate where both of the effects were clearly defined and not interfering. Conversely, if turbulent flow were considered, both the hydrodynamic and the electrokinetic effects may interfere where the turbulent conditions may dwarf the electrokinetic effect. Nonetheless, it is still interesting to look into the turbulence conditions where the electrokinetic material removal process may be further enhanced.

8.3.4 Integration of electrokinetic material removal technique onto existing material removal processes

The schematic setup of the electrokinetic material removal is similar to some of the existing processes (such as electrochemical machining (ECM) [25] and electrical discharge machining (EDM) [25,161]). It would be interesting if the electrokinetic material removal concept can be integrated onto these existing setups such that the electrokinetic material removal process is able to enhance the material removal rate or the surface finish of the workpieces after the integrated processes.

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Appendix A

Equipment used during fabrication process

During research study, several equipments were used for the fabrication of the samples.

And they are as listed:

1. Chemical wet bench for silicon wafer cleaning and resist stripping
2. Furnace for oxidation of silicon wafers
3. Karl Suss VPO primer for HMDS priming
4. Karl Suss spin coater for spin coating
5. Hot plate for baking
6. Karl Suss mask aligner for UV exposure
7. Spin dryer to remove distilled water from the wafer
8. Magnetron sputter system to sputter metallic films onto wafer
9. Technics micro-reactive ion etching system (Series 800-II) for PDMS etching
10. Deep reactive ion etching (DRIE) for the through-hole etching and production of predetermined rough surfaces

1. Chemical wet bench for wafer cleaning and resist stripping

The Si wafer is first immersed in Piranha bath (96% H_2SO_4 and 4% H_2O_2) maintained at 120° for 20 minutes in the chemical wet bench. The wafer is then dipped into the Quick Dump Rinse (QDR) before it is spin dried in the spin dryer.

Chemical wet bench

2. Furnace for oxidation of silicon wafers

The oxidation furnace is used to grow oxide on silicon. The oxidation is performed at high temperature in pure oxygen or in wet oxygen ambient.

Furnace

3. **Karl Suss VPO primer for HMDS priming**

The wafer is inserted into the Karl Suss Delta VPO primer. There, it is purged in N_2 gas and baked at 100°C to remove surface moisture for 60 seconds. Then it is vapour primed in hexamethyldisilazane (HMDS) for 20 seconds, to promote resist adhesion. Finally, it is baked and purged using N_2 gas for another 60 seconds.

Karl Suss VPO primer

4. **Karl Suss spin coater for spin coating**

The wafer is spin coated with positive photoresist (AZ 9260) using the Karl Suss Spin Coater. The coating speed is ramped in steps as the viscosity of the photoresist is very high, and the ramping will ensure an even spreading of the resist. There are basically 4 recipes programmed in the Spin Coater to facilitate to different resist thickness. The recipes are coded 11, 12, 13 and 14 to produce 2.5, 5, 7.5, 9.91 μm thickness of resist respectively.

Karl Suss spin coater.

5. Hot plate for soft baking

The wafer is baked at 110°C for 4 minutes using the hot plate. This process is to remove the solvent, relieve the stress built up after the spin coating and promote adhesion of the resist to the wafer.

Hot plate

6. Karl Suss mask aligner for UV exposure

The wafer is exposed to UV rays using the Karl Suss mask aligner. The wafer is exposed for under 360nm-wavelength UV radiation at intensity of 9.3mW/m².

Karl Suss mask aligner

7. Spin dryer for spin drying

The wafer is spin dried to remove the distilled away from the developed wafer.

Spin dryer

8. Magnetron sputter system for metallic film sputtering

Metallic film sputtering was done by using the Magnetron sputter system (DC/RF).

Magnetron sputter system

9. Technics micro-reactive ion etching system (Series 800-II) for PDMS etching

The Technics micro-reactive ion etching system (Series 800-II) is used for dry etching of PDMS thin films and photoresist. Gas commonly used in the etching process is CF_4 and O_2

Technics micro-reactive ion etching system (Series 800-II)

10. Alcatel deep reactive ion etching system

The Alcatel deep reactive ion etching system is used for dry etching of Si wafer for the etching of through-holes on the Si wafer and for the production of the predetermined rough surface. Gas commonly used in the etching process is SF_6 and C_4F_8 .

Alcatel deep reactive ion etching system

Appendix B

DOE study on the influencing effects on the material removal rate of the electrokinetic material removal process

Factor	Type	Levels	Values
DC electric field strength	fixed	3	0.0, 12.5, 25.0
AC electric field strength	fixed	3	30, 50, 100
AC electric field frequency	fixed	3	7.5, 10.0, 500.0
Fluid velocity	fixed	3	0.2, 0.4, 1.4

Analysis of Variance for Material removal rate, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F
DC electric field strength	2	3349405	3349405	1674703	28.86
AC electric field strength	2	1522172	1522172	761086	13.12
AC electric field frequency	2	2757032	2757032	1378516	23.76
Fluid velocity	2	1289497	1289497	644748	11.11
DC electric field strength	4	1400742	1400742	350185	6.03
*AC electric field strength					
DC electric field strength	4	1453372	1453372	363343	6.26
*AC electric field frequency					
DC electric field strength	4	722755	722755	180689	3.11
*Fluid velocity					
AC electric field strength	4	686365	686365	171591	2.96
*AC electric field frequency					
AC electric field strength	4	218262	218262	54565	0.94
*Fluid velocity					
AC electric field frequency*	4	346049	346049	86512	1.49
Fluid velocity					
Error	48	2785330	2785330	58028	
Total	80	16530981			

Source	P
DC electric field strength	0.000
AC electric field strength	0.000
AC electric field frequency	0.000
Fluid velocity	0.000
DC electric field strength	0.001
*AC electric field strength	
DC electric field strength	0.000
*AC electric field frequency	
DC electric field strength	0.023
*Fluid velocity	
AC electric field strength	0.029
*AC electric field frequency	
AC electric field strength	0.449
*Fluid velocity	
AC electric field frequency	0.220
*Fluid velocity	
Error	
Total	