MOLECULAR MECHANICS SIMULATIONS OF QUARTZ ETCHING PROCESS

by

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LIST OF SYMBOLS

Symbol	Description	Unit
Y_s	Sputtering Yield	amu/atom
$\langle A \rangle$	Indicates time and ensemble average	-
A	Amplitude	m
Å	Angstrom	m
$a(t)$	Acceleration	ms^{-2}
$A(\Gamma(t))$	Function of phase time	-
D	Dissociation Energy	kgm^2s^{-2}
E_i	Incident Energy	kgm^2s^{-2}
E_{surf}	Surface Binding Energy	kgm^2s^{-2}
E_{th}	Threshold Energy	kgm^2s^{-2}
F_i	Interaction Force	$kgms^{-2}$
k	Spring Constant	kgs^{-2}
k_b	Boltzmann constant	$J.K^{-1}$
K_{IC}	Fracture Toughness	-
M_1	Mass of impinging atom	amu
M_2	Mass of target atom	amu
p	Momentum	$kgms^{-1}$
r_o	Initial distance between two atoms.	m
$S_n(E)$	Energy dependent nuclear stopping cross section	kgm^2s^{-2}
T_s	Surface temperature	K
U_b	Sublimation energy	kgm^2s^{-2}
U_d	Lattice Displacement Energy	kgm^2s^{-2}

U_t	sputtering threshold energy	kgm^2s^{-2}
$v(t)$	Velocity	ms^{-1}
$V(x)$	Potential energy	kgm^2s^{-2}
$x(t)$	Position	m
Z_1	Atomic number of impinging atom	-
Z_2	Atomic number of target atom	-
Δt	Time step	s

Greek Symbols

ε	reduced energy
α	Alpha
α^*	Function of mass ratio
θ_i	Incident Angle
τ	coupling constant of $\frac{M_2}{M_1}$
Γ	contribution of B-sputtering mechanism to the total sputtering yield

LIST OF ABBREVIATIONS

BD	Brownian Dynamics
CF_3	Trifluoromethyl
CFD	Computational Fluid Dynamics
CHF_3	Fluoroform
Cl^*	Radical Clorine
Cl_2	Chlorine
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COMB	Second Generation Charge-Optimized Many Body
DFT	Density Functional Theory
DPD	Dissipative Particle Dynamics
eV	Electrovolt
F^*	Radical Flourine
FEA	Finite Elements Analysis
FEV	Finite Volume Analysis
HF	Hydrofluoric Acid
HF	Hatree Fork
I.S.A.A.C.S.	Interactive Structure Analysis of Amorphous and Crystalline Systems
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MC	Monte Carlo
MD	Molecular Dynamics
MEM	Microelectromechanical Systems
NEMs	Nanoelectromechanical Systems

NVE	mol,volume and energy
PBC	Periodic boundaries conditions
PKA	primary knock-on-atoms
QM	Quantum Mechanics
RF	Radio frequency
RIE	Reactive Ion Etching
SF_6	Sulfur hexafluoride
SiO_2	Silicon dioxide
SiO_4	Silicon-Oxygen Tetrahedrate
SPH	Smooth Particle Hydrodynamics
SRIM	Stopping and Range of Ion in Matter
SW	Stillinger-Weber
TRIM	Transport of Ions In Matter
UV	Ultra Violet

SIMULASI PROSES PUNARAN TERHADAP KUARZA MENGGUNAKAN KAEDAH MOLEKULAR MEKANIK

ABSTRAK

Thesis ini membentangkan hasil kajian tentang proses punaran secara fizikal menggunakan hentaman Argon ke atas substrat α-kuarza dan amorfus kuarza dengan menggunakan kaedah molekular mekanik. Walaupun kajian mendalam terhadap proses punaran ke atas kuarza sudah ada, namun kebanyakan daripadanya adalah secara eksperimen dan fokus kajian tersebut hanyalah pada hasil akhir proses tersebut. Terlalu sedikit kajian dijalankan yang menjurus kepada asas dan fundamental proses punaran. Dengan menggunakan kaedah Monte Carlo (MC) dan Molekular Dinamik (MD), para pengkaji dan ahli akademik mampu membina model proses punaran daripada awal hingga penghujung proses tersebut. Teknik ini membolehkan proses ini dikaji di tahap saiz sekecil molekul dan membantu pengkaji memahami teori asas dan fundamental proses punaran terhadap kuarza.

Dua teknik penkomputeran digunakan untuk membina model proses punaran secara fizikal ke atas substrat kuarza. Teknik pertama berdasarkan statisik (teknik Monte Carlo) dan teknik kedua berdasarkan teknik ketentuan (Molekular Dinamik). Untuk teknik Monte Carlo, produk utama yang dicari adalah hasil percikan, Y_s dan pembahagian tenaga pada atom yang terpercik. Selain itu, hubungan antara tenaga tujahan, E_i, sudut tujahan, θ_i kepada hasil akhir juga dibincangkan. Berdasarkan teknik ini, pada sudut tujahan, $\theta_i = 70^o$ dengan sebarang tenaga tujahan, E_i,hasil percikan, Y_s yang dihasilkan adalah maximum.

Teknik molecular dinamik pula melaporkan kesan terhadap punaran secara terpilih, kesan suhu substrat,T_s dan kesan tenaga tujahan, E_i terhadap hasil pemercikan atom dan seterusnya menghubungkan hasil pemercikan atom dengan sifat-sifat subtrak. Objektif utama projek ini adalah untuk mengguna kaedah pengkomputeran bagi membina model proses punaran di skala dalam molekul. Dua jenis substrat yang berlainan (α-kuarza dan amorfus kuarza) digunakan dan substrat tersebut melalui proses hentaman Argon dengan tenaga tujahan, E_i suhu substrat, T_s berlainan secara berkala. Model komputer punaran kuarza menggunakan Potensi Morse dan Potensi COMB (*Charged Optimized Many-Body*) sebagai potensi antara atom.

Berdasarkan kajian yang telah dibuat, α-kuarza menghasilkan pemercikan atom lebih tinggi daripada amorfus kuarza dengan menggunakan mana-mana tenaga tujahan, E_i dan suhu substrak, T_s. α-kuarza juga menghasilkan pemercikan atom yang lebih stoikiometrik berbanding amorfus kuarza. Ini desebabkan untuk α-kuarza produk pemercikan dalam bentuk SiO_2 dan amorfus kuarza dalam bentuk atom. Tenaga tujuhan, E_i menghasilan impak yang lebih besar kepada hasil pemercikan atom berbanding suhu substrak, T_s.

Di dalam kajian ini, model pengkomputeran untuk proses punaran berjaya didemonstrasikan dengan mengunakan kaedah Monte Carlo (MC) dan Molekular Dinamik (MD). Beberapa faktor yang memberi kesan ke atas punaran telah pun dikaji dan pemahamam terhadap proses punaran di skala molekul berjaya ditambah. Hasil kajian dari tesis ini berpotensi untuk digunakan di dalam proses pencorakan untuk fabrikasi nano 2D dan 3D.

MOLECULAR MECHANICS SIMULATIONS OF QUARTZ ETCHING PROCESS

ABSTRACT

In this thesis, the physical etching of argon bombardment onto α-quartz and amorphous quartz substrates were studied and investigated using molecular mechanics methods. Although there are extensive studies on quartz etching, larger numbers of the research are experimental and the studies focus on the process outcomes rather than the fundamental study of the process. Molecular mechanics methods such as Monte Carlo (MC) method and Molecular Dynamics (MD) method enables researchers in building the model from ground up to the physical etching process. This kind of bottom-up design allows us to study the process in molecular level and help researcher grasp the fundamental theory of the process.

Two computational methods have been employed in order to study quartz etching process. The first method are based on statistical approach i.e Monte Carlo and the second method is based on deterministic approach i.e Molecular Dynamics. In Monte Carlo method, the main interest of the simulations is sputtering yield, Y_s and energy distribution of sputtered atoms. The relationship of incident energy, E_i , and incident angle θ_i to the interested subjects will also been investigated and discussed. It was found that at incident angle $\theta_i = 70^o$ at any incident energy, E_i, the sputtering yield, Y_s is maximum.

Molecular Dynamics method reported the effect of etching selectivity, the effect of substrate temperature, T_s, and the effect of incident energy, E_i to the sputtering yield and ultimately corroborates the factor and sputtering yield with the properties of the substrate. The main objective of this project is to use computational method (i.e Molecular Dynamics) to model the process at the scale of molecular level. Two difference substrates (amorphous and α-quartz) are subjected to a range of incident energy. E_i and temperature, T_s and the sputtering yield were studied. Morse potential and Second Generation Charge-Optimized Many Body (COMB) potentials were utilised as the inter-atomic potential.

α-quartz shows higher sputtering yield as compared to amorphous quartz at any given incident energy, E_i and substrate temperature, T_s. α-quartz has also produced more stoichiometric yield compared to amorphous quartz. This is because for α quartz, the sputtered product are in mostly the form of SiO_2 molecule while amorphous substrate the sputtered product in the form of atom. Incident enery, E_i gave significant increase in the sputtering yield compared to temperature, T_s.

In this thesis, the computational model of physical etching on quartz has been demonstrated using the Monte Carlo (MC) method and Molecular Dynamics (MD) method. Several factors are studied and better understandings of the process in molecular level have been achieved. The results of this study could be applied in 2D and 3D patterning used in lithography technique.

CHAPTER 1

INTRODUCTION

1.1 Introduction

For the past 20 years, the demands for micro and nano size devices have increased substantially. Along with the advancement of new technology and scientific research, new methods have been introduced for patterning and fabricating the micro/nano structures.

Many studies have been carried out related to etching process. However most of the studies were performed experimentally which produced results but not fully explaining the fundamental science of the process. These huge vacuums of knowledge on the underlying science of nanofabrication make the process unrepeatable and ultimately make the product from individual experiment cannot be mass produce. Thus, computational aided simulations are essentials to fully grasp the fundamental of the process. However, classical approaches that utilise spatial-temporal analysis i.e Finite Elements Analysis or Finite Volume Method (FEA/FVA) method are insufficient to model nano or meso scale size simulations. This is because the size of individual atoms and molecules are comparable to the overall size of the simulation box thus violating the assumption make when using Navier Stoke's equation. In addition, intermolecular bond and interactions between atoms and molecules are non-trivial, unlike in continuum model where inter-atomic and intermolecular forces are omitted. Hence, to overcome this problem, a novel method is needed. One of the many methods is Molecular Dynamics.

Molecular Dynamics (MD) methods are used to tackle complex problems in nano scale analysis. Numerous researches in materials properties, rheology and tribology had hugely benefited from molecular dynamics simulation works. With the great advancement in computational capability, molecular dynamics has become powerful tools for engineer and scientist.

1.2 Research Background

Nanoscale devices have been hugely benefited by society in wide range of applications. Applications like NEMs/MEMs, microfluidics, nano-optical devices have attracted industry as well as researchers because these applications offer a huge prospect for development. In order to build nanoscale devices, the knowledge in nanofabrication is vital. There are many fabrications techniques and they can be characterized into two categories; wet and dry etching. Wet etching employed chemical or liquid etching for material removal (fabrication) process whilst dry etching process utilised plasmas or etchant gasses for material removal.

One of the most common patterns transferring technique in nano scale is by using reactive ion etching (RIE) method. In this method, continuous bombardments of atoms or ions onto a substrate (e.g quartz) are used as means to fabricating pattern by etching the surface atoms. This technique is also often paired with plasmas or gaseous etching in order to achieve anisotropic or high aspect ratio profile.

Although there are extensive studies have been done relating to RIE, most of the studies are experimental. Often, the results from experimental are cannot explain the fundamental of the process. This is because of the complex behaviour of plasma

etching process. Hence, a computational model is essential in simulating the process and provides useful information in understanding and hopefully predicting the process at molecular level.

In this thesis, an attempt to model quartz etching process using molecular dynamics (MD) and Monte Carlo simulation are presented. In this project, the mechanical or physical process is the main focus rather than the chemical process. This project will study the physical etching roles in the pattern transferring process. The main interests are the analysis of velocity, momentum, force and energy of the quartz etching process.

Molecular dynamics simulation can be divided to three stages. The first stage is to define the system. This include initial conditions (e.g number of atoms, simulation's volume), boundary conditions and inter-atomic potential etc. At stage two, new positions and velocities of atoms are calculated using Newtonian equation. Macroscopic properties such as temperature and stress can be calculated using the updated position and velocity. At stage three, the time averaged macroscopic properties are calculated.

Quartz is chosen as an object of study because of its superiority properties and has huge unexplored potential in MEMS/NEMS. Quartz has superior in hardness, stronger resistance in temperature and higher UV light transmission. Quartz also has unique properties of piezoelectric. High aspect ratio nanostructure on quartz has many applications such as sensor, wave guide and nano-imprint mold.

1.3 Problem Statements

The main objective for nanofabrication methods is to obtain the desired profile within tolerance. However, most of the cases suggest the contrary. There are many factors that can cause the end results deviate from the desired profile. Due to the imaging limitation, the etching process cannot be observed in real time. In order to understand the influencing factors, a computational model is proposed. A computational model enables us to study the etching as the process proceeding. This includes bond breaking, bond formation and sputtering etc.

Etching process occurs at molecular level. Methods that used continuum model such as FEA that used Navier Stoke equation unable to model process at molecular level. Thus, a novel method is required in order to model the process at nano-scale. There are several methods that are available in nano-scale modelling. However the most accurate and deterministic method is Molecular Dynamics (MD) method. In this project, a MD model of quartz etching process will be investigated.

From experimental observations, the main factor that affects etching are energy and temperature. However, proper explanations are unable to be presented because of experimental and imaging limitations. Hence, one way of explaining the factor is by using computational modelling.

1.4 Research Objectives

a) To develop a computational model of the reactive ion etching (RIE) environment for α-quartz and amorphous quartz etching. These include the incident ions with pre-determined velocity, substrate structure, the suitable bonding energy between them and intermolecular forces.

b) To utilize the molecular dynamic (MD) simulation in calculating the trajectories of atom/molecules and properties and its relationship to energy, momentum and temperature.

c) To study the effect of velocity, temperature and selectivity on the etched profile.

1.5 Thesis Outline

This thesis consists of five main chapters. Chapter 1 is the introduction of the thesis. This chapter will give an overview of this thesis and brief introduction to the research scope like the molecular dynamics (MD) methods and physical sputtering in reactive ion etching. A list of problem statements that will be investigated throughout of this thesis will also be presented and the need of the understanding of physical etching behavior in molecular level is thoroughly discussed.

Chapter 2 compiles all the works and research that related to this project. At the beginning of the chapter, the quartz properties and its usages in industry are discussed. The concepts and theory about sputtering were also introduced. These include the physics of ion bombardment and effects of materials properties on sputtering. In this chapter, inter-atomic potentials (i.e Morse potential and COMB potential) used in this study are explained. Lastly, the effect of temperature, energy and selectivity to the sputtering process are presented based on others research and studies.

In Chapter 3, all of the methodology of this research will be presented. These include the details of building the basic structure of α-quartz and amorphous quartz.

The basic structure will be used as a building block to create a giant structure of quartz. The building block of quartz is independently built as a mean to further our understanding on this topic. After the substrates were built, the substrates will undergo several simulation tests. These simulations are conducted to fulfill the objectives of this thesis. Simulations are conducted in two methods which are Monte Carlo (MC) method and Molecular Dynamics (MD) method. The details of the simulations will be covered in details in this chapter.

In Chapter 4, all the results obtained from all the methods explained in Chapter 3 are presented. The results from Monte Carlo (MC) Simulations method are presented at beginning of this chapter as supporting results that are used to explain the results from Molecular Dynamics (MD) Simulation method. MC method will give the results that show the relationship between the incident angle, θ_i with sputtering yield, Y_s and incident energy, E_i with sputtering yield, Y_s. MC method also helps visualize the etching process at molecular level as the process take place. This can be done by plotting the atom/molecule position according to the trajectory calculated using MC method. The etching selectivity between α-quartz and amorphous quartz also were presented in this chapter.

Chapter 5 gives the overall conclusion about this research. Recommendations are also presented for improving future and more extensive research on this subject.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter compiled the works and researches that related to quartz etching. Firstly, the quartz properties and its usages in industry are discussed. Then, the concepts and theories about sputtering are introduced. These include the physics of ion bombardment and the effects of materials properties on sputtering. In this chapter, Morse potential and COMB potential that are employed in this study are explained. Lastly, the effect of temperature, pressure and energy to the sputtering process are studied.

2.2 Quartz properties and its usage in semiconductor Industry

Quartz is the second most abundant mineral found on the earth surface after feldspar and most abundant oxide in earth's crust. Examples of quartz in nature are sand and gemstones. Quartz is made up from silicon-oxygen tetrahedrate, SiO_4. In crystallize silica, one oxygen atom is shared by two tetrahedra (bonded to silicon) which gives the overall molecular formula of SiO_2 (Silicon dioxide or silica).

In old ages, quartz is mostly used for jewelry. However for the past 50 years, quartz has been used extensively in semiconductor industry. For example, in electronic industry quartz are highly desirable for micro and nano device applications. For example, in Spruce Pin, North Carolina in which the only place ultra-pure quartz can be found, the quartz mining there are the main factor that cause the Silicon Valley to flourish.

The main reason quartz are used in semiconductor industry is because of its electrical properties. Quartz glass has high dielectric strength and low conductivity along with its superior thermal and optical properties and UV transmission make Quartz glass suitable for electronics wafer.

Quartz glass or fused quartz or fused silica is formed by melting ultra-pure quartz crystal at a high temperature. This gives rise to an amorphous silica with high melting point and extremely low thermal expansion coefficient of 5.5×10^{-7}/°C (Division, 2009). This enables quartz glass to withstand continuous temperature change and thermal shock without experiencing thermal deformation or cracking.

Quartz glass is chemically inert for most solution except for hydrofluoric acid, HF which contains very reactive fluorine ions that can dissolve silica. Quartz glass can also be formed, cooled and annealed without undergo crystallization first because it has very high viscosity. Quartz glass is also clear and translucent and these give it the property of UV transparency in which very useful in semiconductor industry. **Error! Reference source not found.** shows the engineering properties of fused silica.

2.3 Quartz Etching

In microelectricalmechanical and nanoelectrocmechanical system (NEM and MEM) fabrication, etching is common technique for fabrication in semiconductor industry. Etching by definition is a process by which material is removed from a surface. There are two types of etching used in industry; wet etching and dry etching. By definition wet etching is material removal process that uses liquid chemical or

etchant and dry etching is materials removal process that used etchant gasses i.e Argon or plasmas (Madou, 2002). Wet etching involves chemical reactions that etch targeted surface in the form of etch product while dry etching mainly utilize high kinetic energy of accelerated particle to etch targeted surface by knock atoms off from targeted surface.

Table 2.1 Fused silica engineering properties (Division, 2009)

Fused Silica			
Mechanical	**Units of Measure**	**SI/Metric**	**(Imperial)**
Density	gm/cc (lb/ft^3)	2.2	(137.4)
Porosity	% (%)	0	0
Color	—	clear	—
Flexural Strength	MPa (lb/in^{2}x10^3)	—	—
Elastic Modulus	GPa (lb/in^{2}x10^6)	73	(10.6)
Shear Modulus	GPa (lb/in^{2}x10^6)	31	(4.5)
Bulk Modulus	GPa (lb/in^{2}x10^6)	41	(6)
Poisson's Ratio	—	0.17	(0.17)
Compressive Strength	MPa (lb/in^{2}x10^3)	1108	(160.7)
Hardness	Kg/mm^2	600	—
Fracture Toughness K_{IC}	MPa•m$^{1/2}$	—	—
Maximum Use Temperature (no load)	°C (°F)	1100	(2000)
Thermal			
Thermal Conductivity	W/m•°K (BTU•in/ft^2•hr•°F)	1.38	(9.6)
Coefficient of Thermal Expansion	10^{-6}/°C (10^{-6}/°F)	0.55	(.31)
Specific Heat	J/Kg•°K (Btu/lb•°F)	740	(0.18)
Electrical			
Dielectric Strength	ac-kv/mm (volts/mil)	30	(750)

Dielectric Constant	@ 1 MHz	3.82	(3.82)
Dissipation Factor	@ 1 MHz	0.00002	(0.00002)
Loss Tangent	@ 1 MHz	—	—
Volume Resistivity	ohm•cm	$>10^{10}$	—

Several experimental studies have been done to etch quartz. Studies by Mohamed and Alkaisi (2013)have achieved high aspect ratio of sub-100nm features. The optimized CHF_3/Ar RIE parameters for 2D pattern as shown in Table 2.2

Table 2.2 Oprimized CHF_3/Ar RIE parameters for 2D pattern transfer onto a quartz substrate (Mohamed and Alkaisi 2013).

RIE parameter	Setting/measured
Gases	CHF_3/Ar
Flow rate	50/30 sccm
Pressure	20 mTorr
Temperature	295 K
RF power	200 W
RF power density	2.5 W cm^{-2}
Bias voltage	−330 V
Etch rate	10 nm min−1

2.3.1 Plasma Etching

Plasma by definition is collection of free moving (fluidic) partially ionized particles that have equal number of positive and negative charges which in average electrically neutral. Plasma is one of the states of matter; apart of gaseous, liquid and solid. In controlled container, when we apply voltage or current source as shown in

Figure 2.1, as charged particle drift, it will collide with other neutral particles thus ionized it. This sustainable process occur thus create a steady plasma state inside the container. This phenomenon called plasma discharge.

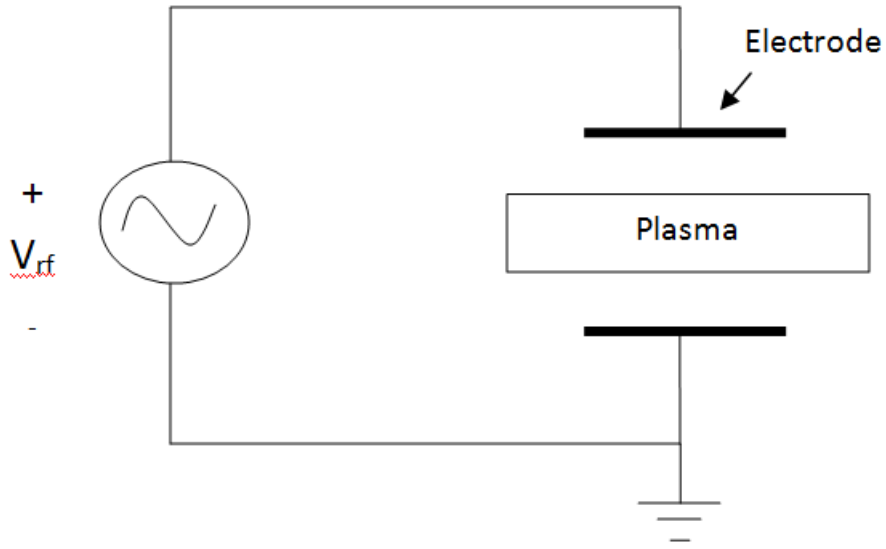

Figure 2.1 Schematic diagram of plasma discharge.

Figure 2.2 show the schematic diagram of plasma etching. Radio frequency, RF or microwave power will accelerate ion towards SiO_2 substrate. With enough energy, the energetic ions will bombard and produce clean cut sidewalls as shown in

Figure 2.3. This kind of etching is called anisotropic plasma etching.

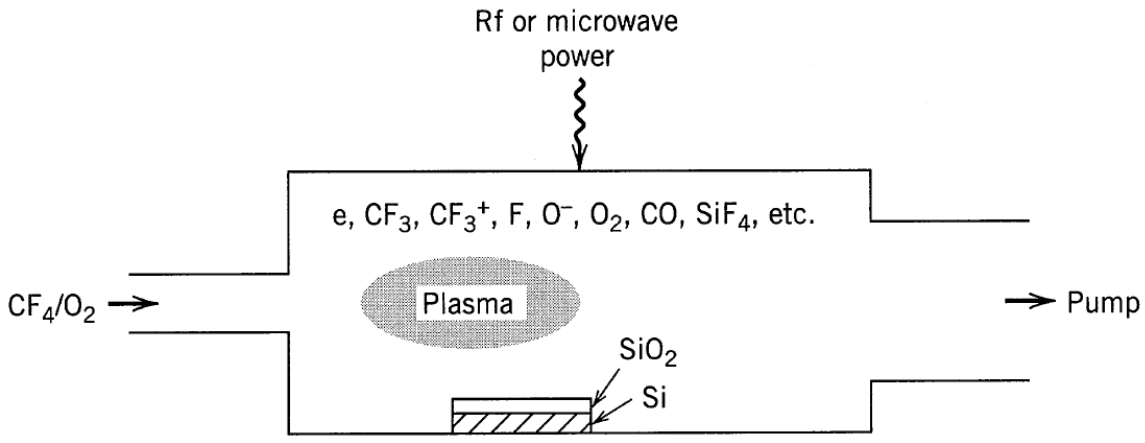

Figure 2.2 Schematic diagram of plasma etching (Lieberman and Lichtenberg, 2005)

In semiconductor fabrication, anisotropic profile is highly desired. Plasma etching are not limited to physical etching only, we can add radical to increase etching process. This technique called Reactive Ion Etching (RIE).

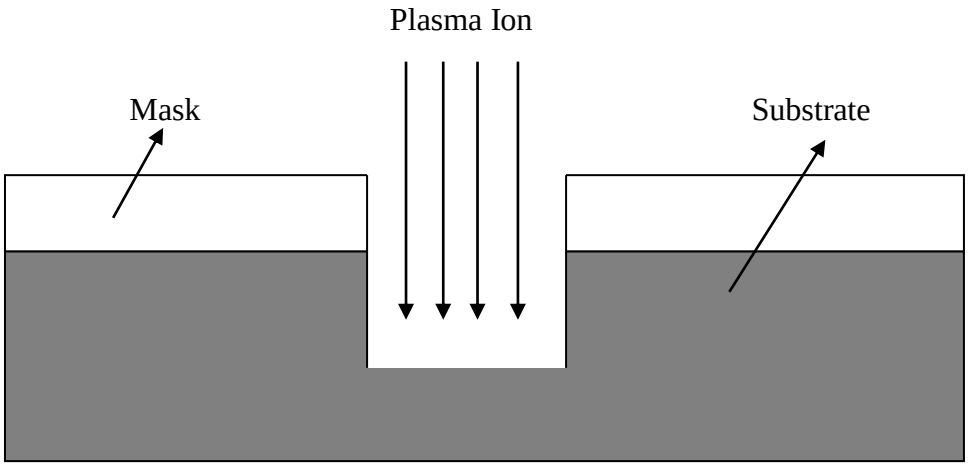

Figure 2.3 Representation of anisotropic etching (Lieberman and Lichtenberg, 2005)

2.3.2 Reactive Ion Etching

Reactive Ion Etching (RIE) is a derivation of plasma etching and widely used in semi-conductor industry. Different with purely plasma etching that used accelerated ion/particle/atoms to etch targeted surface, RIE employ both physical and chemical mechanism to achieve highly anistropic sidewall of etched profile. This makes RIE one of the most efficient method for etching. Apart of physical etching, the accelerated heavy ion i.e Argon will help the chemical etch by facilitating the chemical reaction. The etching process are sometimes too fast it hard to control the process thus damaged the substrate not accordingly to the desired profile.

RIE are designed so that it gave better control to obtain anisotropic profile and higher selectivity. RIE are able to operate at lower pressure hence allowed longer

mean free path for accelerated particle. Typical etchants are CHF_3 ,CHF_4, SF_6, BCl_2 + Cl_2, are used in RIE process. The free radical i.e F^* or Cl^*, are created by plasma discharge and these radical are highly reactive(Ren et al., 1995, Winters, 1978). For quartz (SiO_2) etching the chemical process can be describe as below:

$$e^- + CHF_3 \rightarrow CHF_2^+ + F^* + radicals\ (e.g.\ CF_x) + 2e^- \quad (2\text{-}1)$$

$$SiO_2 + xF^* \rightarrow SiF_x + O_2 \quad (2\text{-}2)$$

$$CF_x radicals + 2O_2 \rightarrow CO + CO_2 + COF_2 \quad (2\text{-}3)$$

As mentioned before, heavy ions are usually accelerated towards substrate to increase and facilitate etching. Apart of physically etch the targeted area, incident particle also help break the Si-O bond, the dissociated silicon ion will reach with free radical to form SiF_x as shown in equation (2-2). The CF_x radicals tend to deposit polymer films on all surfaces, but the oxygen liberated in the etching of quartz reacts with CF_x radicals to form volatile CO, CO_2, and COF_2 as shown in equation (2-3).

In the study of physical etching (no chemical reaction), theory has been formulated in the context of linear cascading collisions with consecutives knock-on – atoms (Kubota et al., 1998, Sigmund, 1981). In RIE, argon is used as a form of carrier to transport etcher like fluorine and chlorine (Yang and Bandaru, 2007). In a mix of physical and chemical etching, Argon was added as heavy gas in order to enhance the etching process as for instance in reactive ion etching. However, because of its inert properties, Argon has no effect the on chemistry of the plasma. Although it is imperative to note that Argon did affect the energy transfer between impinging atom to the substrate (France and Short, 1998, Xiao-Lin et al., 2010). However, this study focus on the physical etching rather than chemical etching. Thus this study is limited to that extent.

2.4 Sputtering

In etching process, sputtering is one of the techniques for patterning or surface erosion. The term sputtering may refer to either:

a) Sputter emission or sputter erosion : the erosion of a surface by particle bombardment (Sigmund, 2011)

b) Sputter deposition : the production of a thin film by deposition of sputtered materials on a substrate (Sigmund, 2011)

In reality, both processes occur simultaneously. However, this study is focused on sputtering emission or sputtering yield. The details of sputtering will be explain in the next session.

2.4.1 Concept and Theory

As mentioned briefly in section 1.4 , this study focused mainly in physical etching. The physical etching process occurs dominantly by sputtering. In plasma etching, heavy ion are usually used as the incident atoms, typically atom in Group 18 of periodic table because they are chemically inert. However regardless of the incident particles are ion, atom or molecules, the most important factor that determine the outcome is the kinetic energy of the incident atom, E_i (Glang, 1970). Incident particles are usually ionized for it to be accelerated through the use of RF voltage. However, the charge carried by the particles are not needed to be considered because as soon it reach the targeted surface, it will discharge and neutralized by field-emitted electron(Glang, 1970).

If the bombarding particle has low kinetic energy, i.e 5eV, it will not cause much damage to the surface. The particle either diffused to the surface or rebound

back from the surface(Glang, 1970). Diffused particle with high potential energy can cause electron excitation and lead to the secondary electron emission. This chemically break the bond between the adsorbed particle thus cause it to evaporate(Glang, 1970).

Etching occurs on the surface of the targeted material. If the bombarding particle has kinetic energy higher than Lattice Displacement Energy, U_d, permanent damage to the material's surface will be inflicted. If the bombarding particle transfer greater energy than Surface Binding Energy, E_{surf} , sputtering will occurred(Biersack, 2003).

2.4.2 Collisions Cascade

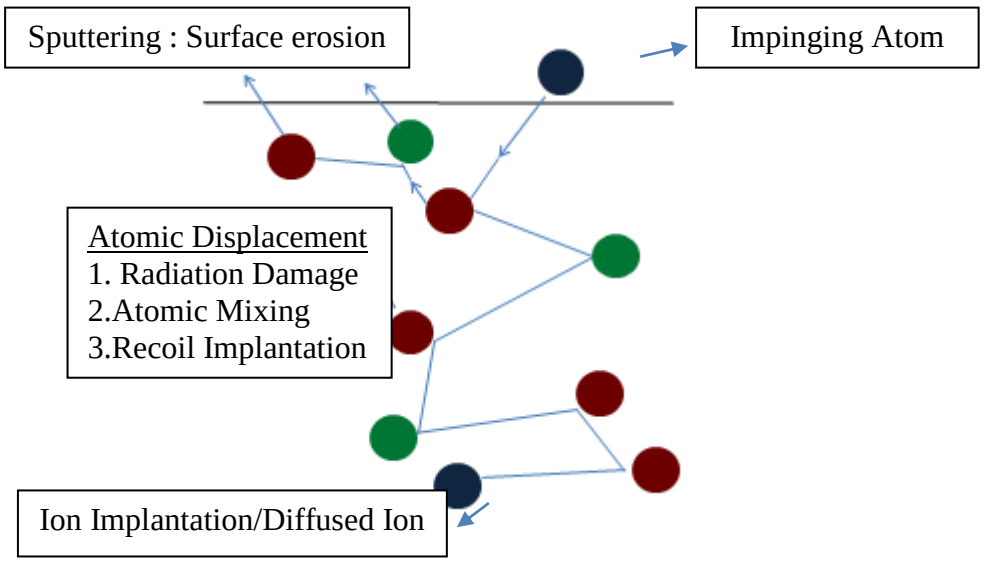

Figure 2.4 Graphic presentation of cascading collisions. Dark blue represent impinging atoms and green and red sphere represent substrate atoms.

Figure 2.4 shows the mechanism of cascading collision and the effects it caused. Cascading collisions occur when an energetic particle (i.e dark blue sphere in

Figure 2.4) induced collisions of adjacent atoms as it diffused into the lattice structure. If the colliding atoms have higher energy than the threshold displacement energy of the material, the collisions can cause permanent displacements. Cascading collisions are the main cause to physical sputtering occurrence. Cascading collisions not only cause surface erosion, but also disrupts and weakened the structure's substrate.

Although by introducing new particles in the substrate can sometimes increase the strength and toughness of the materials but when a continuous bombardment at the same spot will cause surface erosion by removing the dangling atoms. This will facilitate the continuous etching as more energetic particles bombarded onto the substrate.

In Figure 2.4 shows a linear cascading collision. However, for a dense substrate with complex many body potential cascading collisions become extremely complicated. Thus, to model such complex behaviors, molecular dynamics is employed to capture and calculate the trajectories of all the cascading collisions. Figure 2.5 shows the simple illustration of sputtering. The blue ball represent target surface atom and the red ball represent the impinging atom. The four springs that attached to blue ball represent the interatomic potential that holds the blue ball in the space. If the energy transferred from the red ball to the blue ball is large enough, the kinetic energy transferred can overcome the interatomic potential hence trigger sputtering.

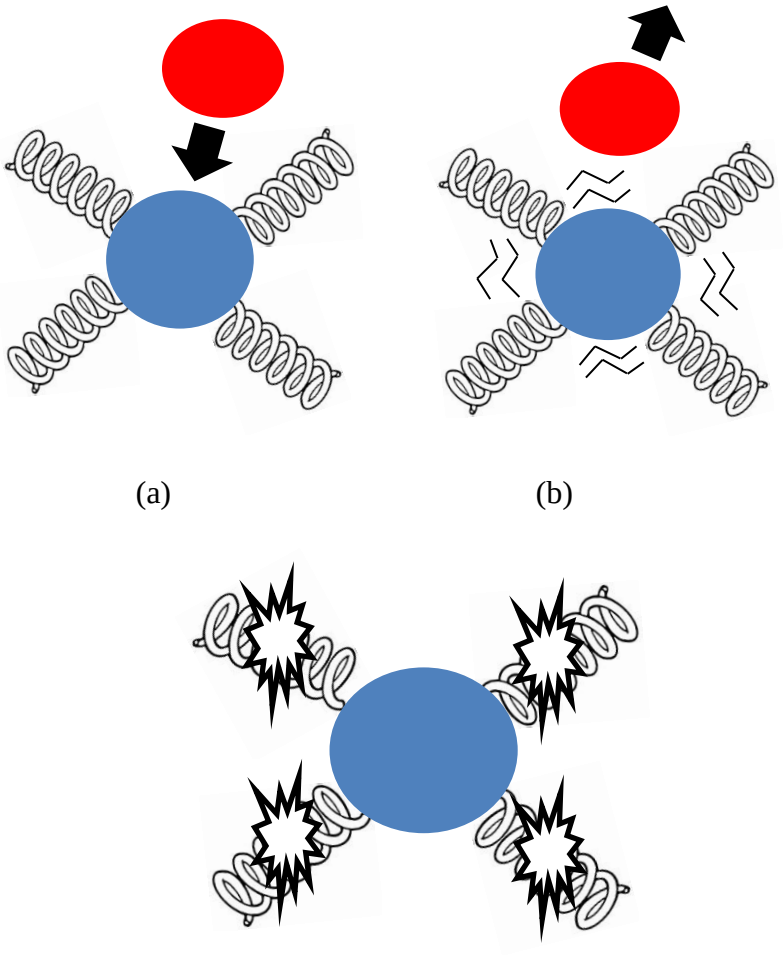

Figure 2.5 Simple illustration of sputtering process (surface erosion).

2.5 α-Quartz

In ambient conditions, quartz is the only stable form of crystalline silica. There are many forms of crystalline (polymorphs) of silica; however, under normal condition, the most common form of polymorphs is α-quartz.(Le Page and Donnay, 1976, Wright and Lehmann, 1981)

α-quartz has a rhombohedral lattice system with the trigonal crystal system as shown in Figure 2.6 and Figure 2.7. Below are the structural parameters for α-quartz.

- Structure: **Trigonal**
- Point group : **32**

- Space group : **$P3_2$ 21 (No.154)**
- Unit cell parameters : **a=b=4.9134 Å ; c=5.4052 Å ; α=β= 90° ; γ=120°**
- Number of Formula Units per cell, **Z=3**
- Density (calculated) : **2.648 g/cm^3**
- Density (measured) : **2.65 g/cm^3**
- Atomic positional parameters (Kihara, 1990)

Table 2.3 Atomic coordinates for quartz in room temperature (298K)

Atom	x/a	y/b	z/c
Si	**0.4679**	**0**	**0**
O	**0.4133**	**0.2672**	**0.1188**

There are also slight derivations in unit cell parameters by other research. For instance unit cell parameter developed by L.Levien *et al* (Levien et al., 1980) shown in Table 2.4 has the c-value are slightly higher than the parameter found Kihara (Kihara, 1990) shown in Table 2.3.

Table 2.4 Unit cell parameter of quartz at pressure 1 atm by (Levien et al., 1980)

	a (Å)	c (Å)	v (Å^3)
1atm	4.916 (1)	5.4054 (4)	113.13 (3)

Table 2.5 Positional and thermal parameters of quartz at pressure 1atmshows the positional parameters and lattice spacing of atoms in α-quartz unit cell at 1atm.

Table 2.5 Positional and thermal parameters of quartz at pressure 1atm (Levien et al., 1980)

Atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Si	0.4697	0	0	0.0093	0.0078	0.0049	0.0039	-0.00001	-0.00002
O	0.4135	0.2669	0.1191	0.0190	0.0144	0.0083	0.0106	-0.00250	-0.00355

By using the configuration we can built quartz unit cell in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) programming. Figure 2.6 shows the crystal structure of quartz α-quartz unit cell at room temperature which has trigonal crystal system in the rhombohedral lattice structure.

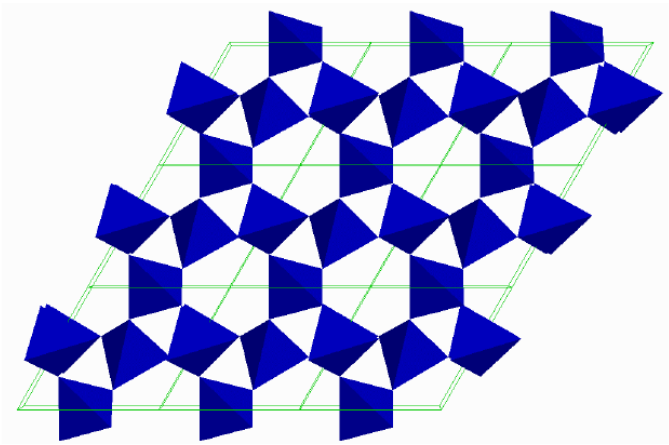

Figure 2.6 The crystal structure of quartz

As mentioned earlier, α-quartz has trigonal crystal system in the rhombohedral lattice stucture. In most silica, one silicon atoms are surrounded with 4 oxygen atoms. Figure 2.7 shows the crystal structure of quartz. In central tetrahedron, one silicon atom shared with 4 oxygen atoms whilst 2 face-centered tetrahedron shared two oxygen atoms with other tetrahedron and the 4 edge-centered tetrahedron shared just one oxygen atom with other.

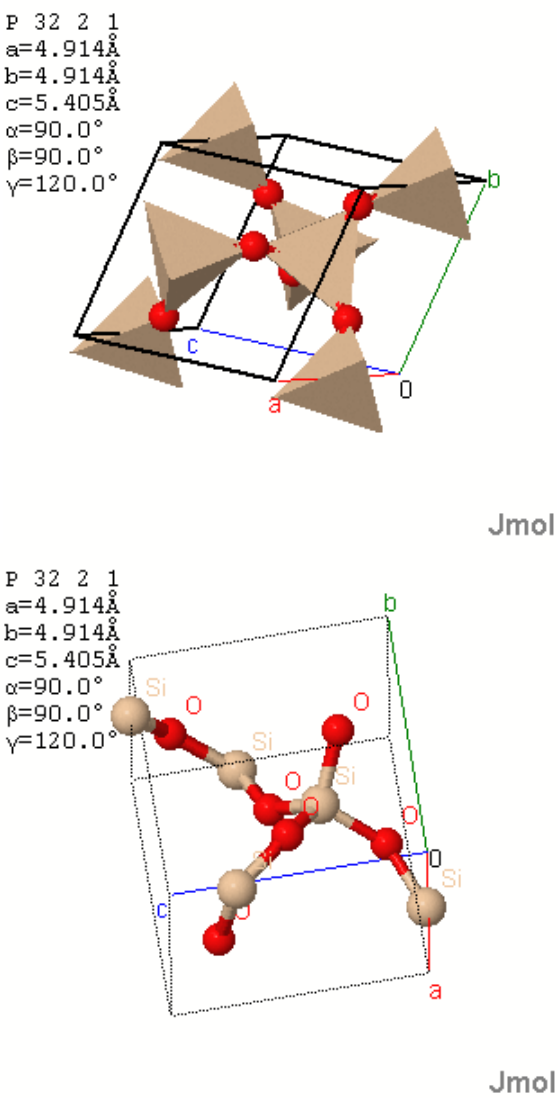

Figure 2.7 3D representation of quartz unit cell (Kihara, 1990)

2.6 Potentials

In molecular dynamics simulations, the most crucial part is to find the appropriate potential to model the system. Potential is set of parameter of formula that describe how the atoms interact. Potential also can be referred as force field. Often, different potential give difference results. Thus, it is very important to understand the potential that we applied.

In molecular dynamics simulations, potentials are developed by these three methods:

1. Empirical method
2. Ab-initio method
3. Semi empirical method

Empirical method uses the existed molecular mechanics potential and the suitable parameters can be found empirically such as Van der waals potentials and Morse potential. Ab-initio is a method that derives computational model directly from the theoretical principles. Ab-initio method gives mathematical approximation of the quantum mechanical of the system. Some of the famous ab-initio method is DFT (Density Functional Theory) and HF (Hatree Fork) calculation. Semi-empirical method are the combination of empirical and ab-initio method.

In this study, two potentials will be utilized;

1. Morse Potential
2. COMB potentials

Morse Potential is based on pair potential whilst COMB potential is base on many body potential. Both potential has shown good results in modeling SiO_2 subtrate. The details of how and why these two potentials will be covered latter in the next section.

To fully understand the sputtering process, thorough knowledge in quantum mechanics is pre-requisite. However, any discussion, experimental, computational modeling or any work related to quantum mechanics are beyond the scope of this thesis.

To understand the concept of potentials, the dynamic motion of chemical bond can be simply described by using the classical model of vibration. Consider a system with harmonic vibrational motion. Base on Newton's equation for harmonic oscillator with initial position zero can be describe by following equation

$$\text{Position; } x(t) = A\sin\omega t \tag{2-4}$$

$$Velocity;\ v(t) = A\,\mathrm{w}\cos\omega t \tag{2-5}$$

$$Acceleration;\ a(t) = -A\omega^2 sin\omega t \tag{2-6}$$

where *x(t)* is position at any given times, *v(t)* is the velocity at any given times and *a(t)* is the acceleration at any given times. A is the amplitude of the vibration where A is the change between initial position, x_o and stretched position, *x ie.* $A=(x_o-x)$. Based on equation of spring:

$$E = \frac{1}{2}k(x_o - x)^2 \tag{2-7}$$

where *E* is kinetic energy, *k* is spring constant, x_o is initial position and *x* is stretched position

A can be describe as:

$$A = \sqrt{\frac{2E}{k}} \tag{2-8}$$

ω is the angular velocity based on Newton's Law and Hooke's Law

$$\omega = \sqrt{\frac{k}{m}} \tag{2-9}$$

where *m* is the mass

In classical mechanics, momentum, $p=mv$, thus from kinetic energy equation

$$E = \frac{1}{2}\frac{p^2}{m} \tag{2-10}$$

From equation kinetic energy:

$$E = \frac{1}{2}\frac{p^2}{m} \tag{2-10}$$

total energy of a system with harmonic oscillator can be describe as:

$$E_{Total} = \frac{1}{2}\frac{p^2}{m} + V(x) \tag{2-11}$$

where *V(x)* is potential energy.

2.6.1 Morse Potential

Based on equation (2-10), if the vibration motion of an atom is model based on harmonic oscillator, the equation will be quadratic. Hence, potential that base on harmonic oscillator would never leads to dissociation. However, in reality, bonds are broken dynamically. A potential has been proposed by Morse (Morse, 1929) that realistically model bond breaking.

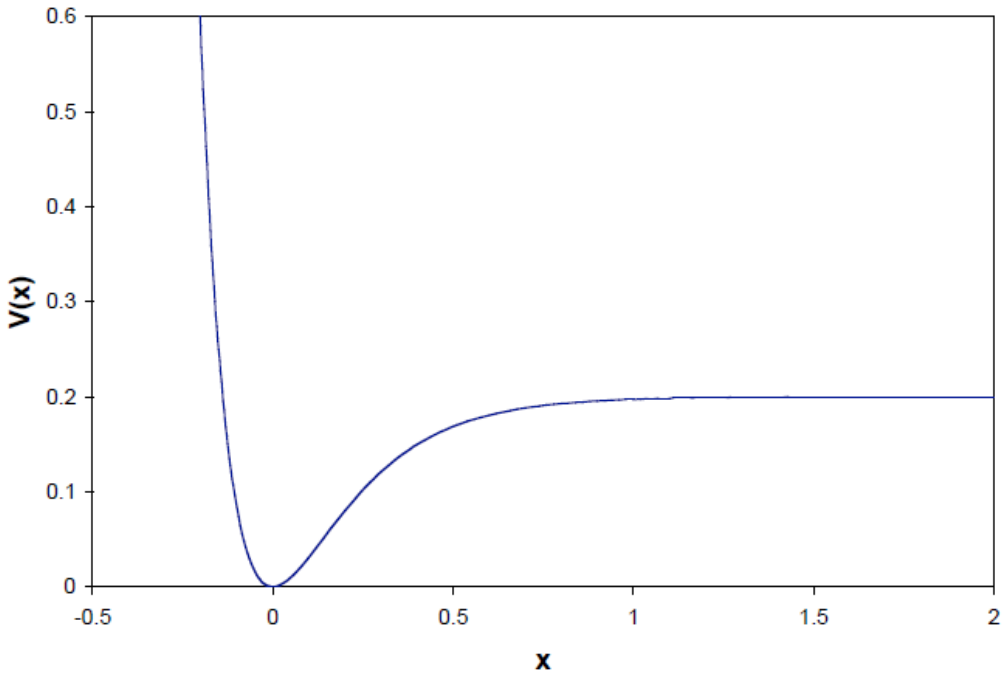

Figure 2.8 Graphical representation of Morse potential

From Figure 2.8, it can be observed that at high x (distance between two atoms), the graph constant indicates dissociation. Graph in Figure 2.8 is represented by the equation :

$$V(x) = D[1 - e^{-a(r-r_e}]^2 \quad (2\text{-}12\ )$$

where *D* is the dissociation energy and *a* is the harmonic frequency of the model and $r_e = \frac{r-r_o}{r_o}$ where r_o is the initial distance between two atoms.

Since the zero potential of diatomic system is arbitrary value, equation

$$V(x) = D[1 - e^{-a(r-r_e}]^2 \quad (2\text{-}12\ )$$

can be re-written as

$$V(r) = De^{-2a(r-r_o)} - 2De^{-a(r-r_o)} \quad (2\text{-}13)$$

Many studies have been conducted that used Morse potential to model quartz. For instance, study by Demiralp *et al* (1999) used Morse potential to study the phase transition of Quartz-Stishovite. Several studies show deviation in Morse potential parameter for Si/SiO_2 systems. For instance Ersan *et al* (1997) have developed the new interatomic potential for silicas based on Morse potential for short range interactions.

2.6.2 COMB Potential

Pair potential such as Morse potential is widely used because of its simplicity and required minimum amount of computational capability. Pair potential is good to be utilized in simple atoms, highly ionic system and gaseous system.

Tersoff (1988b) in his famous paper, *New Empirical Approach For the Structure And Energy Of Covalent Systems*, has proposed a new potential for Si/SiO_2