MOLECULAR MECHANICS SIMULATIONS OF QUARTZ ETCHING PROCESS

by

ABDUL HAADI BIN ABDUL MANAP

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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.