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FORMATION OF MICROSCALE AND NANOSCALE STRUCTURES ON SURFACE IRRADIATED WITH ENERGETIC BEAMS

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**SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2006

Formation of Microscale and Nanoscale Structures on Surface Irradiated with Energetic Beams

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Summary

Very small (microscale or nanoscale) structures, which are the building blocks of future technologies, are very difficult to fabricate by conventional materials processing methods. The project aimed to explore use of energetic beams, mainly focused ion beam (FIB), as a tool to produce microscale and nanoscale periodic structures. A wide range of materials, including pure metals (Sn and Ti), thin film (ZnO) and semiconductors (Si, InP and GaAs), were studied in order to gain a good understanding of ion-solid interactions during fabrication using FIB.

When highly focused ion beam is programmed to erode materials in selected areas by sputtering, nanoscale surface structures may be “written” directly. The use of bitmap and negative beam spot overlap have been demonstrated to be successful methods to control FIB for one-step maskless fabrication of nanoscale pillars and gratings; however, most part of the project dealt with alternate approach to surface nanopatterning that employs ion-induced self-organization. Rastering the surfaces evenly, rapidly and repeatedly at various FIB incidence angles creates ripples or dots on surfaces of the materials. *In-situ* real-time secondary ion and secondary electron imaging were used to follow the evolution of surface features from a low dose of about 10^{16} ions/cm² to a high dose of above 10^{18} ions/cm² and characterized the final surface morphology *ex-situ* using atomic force microscope.

In contrast to usual expectation that surface topology produced at normal ion beam incidence consists of hillocks or depressions, periodic ripples were observed on Sn and Ti surfaces irradiated with FIB. Evidences show that the ripples form spontaneously rather than by “direct writing” of the FIB. Ripples on surface of any single crystal are oriented in the same direction, but the ripple orientation changes with the crystallographic orientation of the sputtered Sn or Ti crystal surface. The observation was explained using a model which attributes the ripple formation to the anisotropic surface diffusion. When the ion beam is tilted by various angles, the ripple orientation is always determined by the crystallographic direction for low-melting point metal Sn. However, for high-melting point metal Ti, the ripple orientation is determined by the crystallographic direction only when the FIB incidence angle is small and curved ripples occur when the angle increases to 45° and above. No existing models can explain the morphological evolution from the well developed straight ripples to the curved ones. A new model was proposed, which attributes the formation of curved

ripples to competition between the formation of ripples due to anisotropic surface diffusion and the formation of incident-angle dependent Bradley-Harper type ripples.

Self-organized ripples were observed on the surfaces of ZnO, Si and InP but not on GaAs. The orientation of ripples is perpendicular to ion beam projection direction, as predicted by Bradley-Harper model for broad ion beam irradiation. However, in contrast to the phenomena commonly observed under broad ion beam irradiation, it is interesting to observe that the surface rippling under FIB irradiation occurs only at certain beam incidence angles, which are between 45° and 60° for ZnO thin film and 30° for both Si and InP. The observation is useful to FIB nanofabrication because it gives information on how to select FIB incident angle properly either to avoid the self-organized surface structures if they are unwanted or to induce them spontaneously if they are desirable.

A noteworthy observation is that ripples on Si rotate from the direction perpendicular to ion projection to a different direction neither perpendicular nor parallel to ion projection when the ion dose increases to 5.19×10^{17} ions/cm². This observation is of great significance, because rotated ripple structures are predicted theoretically but have never been observed before in any experiment.

Another significant observation is that dwell time has considerable influence on surface patterns and sputtering yield of Sn and Si. That means that this FIB parameter can be tuned to increase productivity in FIB nanofabrication or to produce different surface morphology. A new model is proposed to explain the observed increase in sputtering yield with increasing dwell time.

EDX analyses of the FIB sputtered compound semiconductors show that P is preferentially sputtered from InP and As is preferentially sputtered from GaAs. The supersaturation of implanted Ga ions contributes to the formation of metallic Ga droplets on irradiated GaAs surface. Bitmap patterning and *in-situ* FIB imaging reveal Ga redeposition, coalescence and annihilation on the FIB irradiated GaAs surfaces.

List of Abbreviations and Symbols

a	Penetration depth of ion
AFM	Atomic force microscope
C_0	A constant proportional to the square of the effective radius of the interatomic interaction potential
D_s	Surface diffusion constant
D_x	Ion induced effective diffusion along x axis
D_y	Ion induced effective diffusion along y axis
EBSD	Electron Backscatter Diffraction
EDP	End Point Monitor
E_d	The activation energy for surface diffusion of the adatoms
E_i	The energy transferred from the ion to the surface atom
E_o	Total energy at an arbitrary point O contributed by all the ions deposited within the range of the distribution
FIB	Focused ion beam
J	Flux of bombarding ions
K	Relaxation rate due to surface diffusion
k_c	Fourier mode whose amplitude exponentially dominates all the others
ℓ_c	Ripple wavelength
MCP	Microchannel plate
min	Minutes
mm	Millimeter
n	The number of molecules or atoms per unit area on the surface
nm	Nanometer
p	Material constant depending on the surface binding energy and scattering cross-section
R	The region of all points at which the deposited energy contributes to E_o
R_p	Projected range
ΔR_p	Projected range straggling
SEM	Scanning Electron Microscope
T	Temperature

TEM	Transmission Electron Microscope
V_0	The normal erosion velocity at point O
Y	Sputtering yield
Y_1	The number of adatoms created per incident ion
Z'	The distance from point P (start point) to point O (stop point) measured along the ion trajectory
δ	Surface azimuthal orientation
ϵ	Total energy carried by the ion
$\eta(x, y, t)$	An uncorrelated white noise with zero mean accounting for the stochastic arrival of ions to the surface
$\Phi(r)$	Local correction to the uniform flux J due to variation of the local slopes
γ	The surface free energy per unit area
λ_x	The tilt-dependent erosion rate along x axis, depending on flux J and the penetration depth a
λ_y	The tilt-dependent erosion rate along y axis, depending on flux J and the penetration depth a
μ	The width of the energy distribution in direction perpendicular to the incoming beam
μm	Micrometer
ν	The largest in absolute value of the two negative surface tensions ν_x and ν_y
$\nu_x(\theta)$	The effective surface tensions along x axis generated by the erosion process
$\nu_y(\theta)$	The effective surface tensions along y axis generated by the erosion process
Ω	The atomic volume
θ	The incidence angle of the ions
σ	The width of the energy distribution in direction parallel to the incoming beam
τ_1	Characteristic time for an adatoms to diffuse to vacancy or other surface trap
τ_2	Characteristic time for two adatoms to impinge

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Chapter 1 Introduction

1.1 Background

Controlling and manipulating surface morphology on microscale and nanoscale is important for many present and future technological applications (Chason and Aziz, 2003). Energetic beams of various types (electrons, atoms, ions and photons) have been used in the past either to carry out micromachining and nanofabrication directly or to induce self-organization of periodic structures on surfaces (Ghoniem *et al.*, 2002; Her *et al.*, 2000).

In the current project, both femtosecond laser and focused ion beam (FIB) were used to study the interaction between energetic beams and materials. The extremely short pulse duration and very high peak intensity of femtosecond laser differentiate it from conventional pulsed lasers (Liu *et al.*, 1997). Femtosecond laser irradiation is a non-thermal process (Sundaram and Mazur, 2002) and has the capability to ablate materials precisely with little or no collateral damage (Shirk and Molian, 1998). Considerable results have been obtained using FIB. Therefore the dissertation only concentrates on the experimental work carried out using FIB. Selected results for femtosecond laser irradiation of InP are presented in Appendix A.

Surfaces often roughen dramatically with the formation of periodic patterns (ripples, dots and holes) during ion sputtering of the solid surface. Ion beam induced spontaneous

pattern formation was first reported on glass in the 1960's (Navez *et al.*, 1962). Ion beams have been successfully used in alignment of inorganic materials for liquid-crystal displays (Chaudhari *et al.*, 2001) and manufacturing single-digit nanopores (Li *et al.*, 2001). There are also many potential applications for ion induced periodic structures. Ion-induced ripple formation could be advantageous for manufacturing of diffraction gratings used in the wavelength ranging from ultra-violet to x-ray because the gratings could be produced with small wavelengths in a cost effective way. Sputter-induced ripple pattern can also be used for nanoscale wire formation, as proposed in a recent paper (Kim *et al.*, 2002). Other possible technological applications are as varied as optical devices, strain-free patterned substrates for the heteroepitaxial growth of quantum wires, and the tribological films for control of the local roughness on the nanometer scale in the field of surface coatings (Rusponi *et al.*, 1999). In addition, dot arrays patterned on the nanometer scale hold promise for many applications, such as optical devices, DNA or protein and catalysts (Shin *et al.*, 2002).

The evolution of surface morphology during ion sputtering is a complex phenomenon (Kahng and Kim, 2004). Pattern formation on ion irradiated surfaces is dependent on a wide range of incident ion and substrate parameters. These variables include incident ion mass, species, energy, azimuthal angle, incidence angle, flux, fluence and substrate mass, species, crystallographic orientation and temperature. Ion-induced periodic structures are generally thought to be produced as a result of the interplay between a roughening process dependent on surface curvature and a smoothing process by surface diffusion (Bradley and Harper, 1988).

Most experiments on ion-material interaction, including those mentioned above, were carried out with broad ion beam. Compared with broad ion beam, focused ion beam (FIB) has much higher current density and much smaller beam size down to 6 nm. Due to the tiny spot and high current density of a focused ion beam, the desired structures can be directly produced without masks. FIB has found applications in micromachining (Gamo and Namba, 1990; Walker *et al.*, 1996), implantation (Steckl *et al.*, 1995), failure analysis (Burmer *et al.*, 1998; Varkleij, 1998) and TEM sample preparation (Giannuzzi and Stevie, 1999; Overwijk *et al.*, 1993; Sugiyama and Sigesato, 2004). Recently FIB induced periodic structures have drawn much attention to meet requirements of nanofabrication.

Although ion-solid interactions have been extensively investigated for broad ion beam irradiation, certain aspects of the interactions are unique to focused ion beam bombardment (Cuenat and Aziz, 2002) and warrant further study. Dwell time and overlap are two important parameters unique to focused ion beam technique, however their effects on pattern formation or sputtering yield have been rarely investigated.

1.2 Objective and Scope

In view of complicated rippling phenomena and requirement of nanofabrication, a comprehensive and systematic investigation was carried out on the issue of self-organization using focused Ga^+ ion bombardment, involving studying of effect of materials selection and critical experimental parameters, *etc.* The main objective of this

project was to understand the phenomena related with FIB irradiation of various materials over a wide range of experimental conditions, demonstrate a better understanding of the processes involved and serve for nanofabrication.

The main scope of this study include:

- (1) Investigating the effect of experimental parameters (incidence angle, ion dose, dwell time, beam overlap) and the role of material characteristics on self-organized pattern (ripple or dot) formation.
- (2) Studying effect of dwell time on sputtering yield for different materials and proposing new model to explain the phenomenon.
- (3) Designing experiments to testify phenomena that have been predicted theoretically but never proven experimentally.
- (4) Exploring the method for one-step maskless nanofabrication using bitmap patterning.
- (5) Characterizing surface morphology and analysing chemical composition after ion beam irradiation.
- (6) Refining current theoretical models of broad ion beam induced pattern formation to better understand the fundamental rippling mechanisms on various materials (metals, semiconductors or thin film).
- (7) Carrying out Monte Carlo simulation to verify empirical experimental results.

1.3 Layout

The thesis is organized as follows: Chapter 2 reviews ion sputtering mechanisms, models on formation of ion-induced surface patterns and major experimental observations. Chapter 3 describes FIB technology, sample preparation methods and various characterization techniques used in the project. Chapter 4 reports ripple formation on low-melting-point metal Sn surfaces. The effects of incidence angle, crystallographic orientation, dwell time and ion dose on ripple formation were investigated. Chapter 5 explores ripple formation on high-melting-point metal Ti surfaces. The effects of incidence angle, crystallographic orientation and ion dose on ripple formation were investigated. Chapter 6 presents pattern formation on ZnO thin film. Chapter 7 shows pattern formation on elemental semiconductor Si surface. Chapter 8 discusses pattern formation on compound semiconductors (InP and GaAs). Both the surface morphology and chemical composition change were studied. Lastly, Chapter 9 summarizes the experimental results and makes recommendations for further research.

Chapter 2 Literature Review

2.1 Introduction

The chapter aims to survey literature related to ion sputtering and ion-induced formation of patterns on surfaces. The classical theory on ion sputtering is reviewed in Section 2.2 first, with attention paid to curvature dependent sputtering yield and the surface roughening resulted from it. Other factors, *e.g.*, surface binding energy, ion energy, incidence angle and crystal orientation, influencing sputtering yield are discussed in Section 2.3. The ion-induced instability can be mitigated by surface smoothing mechanisms including thermal and irradiation induced atomic transport, as described in Section 2.4. The Bradley-Harper (BH) model is derived based on the competition between ion-induced roughening and surface smoothing, explaining well the formation of surface periodic structures, as discussed in Section 2.5. The BH model is then extended in Section 2.6 to include higher-order spatial derivatives of local surface height, the effects of ion mediated surface relaxation and the stochastic nature of the sputtering process. Section 2.7 briefly describes experimental observations of pattern formation. Surface anisotropy and Ehrlich-Schwoebel barrier are specifically introduced to extend the nonlinear theory to explain the results on metal surface. Finally, Monte Carlo simulation of ion/solid interaction using SRIM (the stopping and range of ions in matter) is discussed.

2.2 Theory of ion sputtering

Sputtering is the removal of material from solids through the impact of energetic particles (Behrisch and Wittmaack, 1991; Townsend *et al.*, 1976). The phenomenon of ion sputtering was first observed by Grove (1853) in a gas discharge as the erosion of the cathode that was bombarded by energetic ions from the plasma. Early theories assumed a thermal mechanism until Wehner (1956; 1960) made two key observations. First, the angular distribution of sputtered atoms for single crystals was highly anisotropic (Wehner, 1956). Surface melting was not involved. Second, Wehner (1960) determined that the energies of the sputtered particles had values of several electron volts, well above reasonably expected thermal energies. Today sputtering has been widely used in a large number of applications, *e.g.*, surface analysis, depth profiling, sputter cleaning, micromachining and coating deposition (Makeev *et al.*, 2002).

When a solid material is bombarded with an ion beam, a number of mechanisms operate to slow the ion and dissipate the energy. These mechanisms can be subdivided into two general categories (Giannuzzi and Stevie, 2005): (i) nuclear energy losses, and (ii) electronic energy losses. Nuclear energy transfer occurs in discrete steps as the result of elastic collisions where energy is imparted from the incident ion to the target atom by momentum transfer. Electronic energy losses occur as the result of inelastic scattering events where the electrons of the ion interact with the electrons of the target atoms.

In the sputtering regime it is nuclear energy loss that dominates the ion/solid interaction.

Three types of ion-nuclear processes can be distinguished (Behrisch and Wittmaack, 1991; Bevolo, 1989), as illustrated in Figure 2.1.

The first type, called single knock-on, is due to the removal of a surface atom by a binary collision with the primary ion (Figure 2.1(a)). The collision cascades are very dilute and involve only a few atoms. The single knock-on usually occurs to low-energy and light-ion bombardment (Behrisch and Wittmaack, 1991; Bevolo, 1989).

The second type of ion-nuclear scattering involves the production of a cascade of displaced target atoms generated by the path of the ion through the solid (Figure 2.1(b)). A basic assumption for a linear cascade is that each atom displaced comes to rest before being struck by another primary ion. Linear cascade occurs under bombardment with ions of medium or high mass at energies exceeding a few keV (Behrisch and Wittmaack, 1991; Bevolo, 1989).

The third type of ion-nuclear interaction is called a thermal spike which occurs when the majority of atoms struck by a primary ion are still in motion from previous ion induced displacements (Figure 2.1(c)). Thermal spike occurs upon bombardment with ions of high atomic number, or with ions of sufficiently high energy (above about 100 keV), and with target atoms of high atomic number (Behrisch and Wittmaack, 1991; Bevolo, 1989).

Figure 2.1 Three types of ion/solid interactions that can lead to sputtering. (a) Knock-on. (b) Linear cascade. (c) Thermal spike. (Bevolo, 1989)

It is the ion induced collision cascade that serves as the core phenomenon. Other beams such as photon and electron beams can induce erosion of a solid but the mechanisms, in most cases, do not involve the collision cascade because of the small mass of the bombarding particles.

A qualitative picture of the sputtering process is as follows (Carter, 2001; Makeev *et al.*, 2002):

When an ion impacts on a surface, if its energy is sufficient to overcome the repulsive potential energy barrier presented by the surface atoms, it will penetrate into the solid and undergo a series of collisions with the atoms of the solid. The ion will first be deflected by its collision with a surface atom and lose some of its energy. It will then continue into the solid, losing energy in further collisions and being further deflected, and will eventually come to rest when its kinetic energy is no longer sufficient to surmount the internal energy barriers. A vacancy and a dynamic recoil atom can be created at each collision. A vast majority of atoms will not gain enough energy to leave their lattice positions permanently. However, some of them will be permanently removed from their equilibrium positions. The atoms located in the close vicinity of the surface, which can gain enough energy to break their bonds, will be sputtered.

A quantitative description of the process of ion sputtering was developed by Sigmund (1973). Sigmund described the sputter process in terms of the energy deposited by the

ion as it slows down through a series of collisions in the solid. In view of the statistical result of a large number of ion collisions, Sigmund proposed that the energy is deposited in 3D ellipsoidal Gaussian contours around the end of the ion track. Since ion entrance positions into the solid will be statistically distributed, individual ion trajectories, stopping positions and details of the collision volume will also be statistically distributed. The volume occupied by these ballistic processes depends upon ion energy, ion mass and target atom mass.

In Sigmund's approach to sputtering, the rate at which material is sputtered from a point on an arbitrary surface is proportional to the power deposited there by the random slowing down of ions. The ion deposited at a point P inside the bulk of the material spreads its kinetic energy density according to the Gaussian distribution (Sigmund, 1973),

$$E(r) = \frac{\varepsilon}{(2\pi)^{3/2} \sigma \mu^2} \exp \left\{ -\frac{Z'^2}{2\sigma^2} - \frac{X'^2 + Y'^2}{2\mu^2} \right\} \quad (2-1)$$

where Z' is the distance from point P to point O measured along the ion trajectory, and X' , Y' are measured in the plane perpendicular to it (Figure 2.2); ε denotes the total energy deposited and σ and μ , are the widths of the distribution in directions parallel and perpendicular to the incoming beam direction, respectively.

Figure 2.2 Schematic illustration of the energy distributed by an incident ion. According to Sigmund model, the ion penetrates the bulk of the material and stops at point P, where all its kinetic energy is released and spread to the neighbouring sites following a Gaussian form with widths σ and μ . (Makeev *et al.*, 2002)

Equation (2-1) describes the effect of a single incident ion. Actually, the sample is subject to a uniform flux J (ions/cm²) of bombarding ions, penetrating the solid at different points simultaneously, such that the erosion velocity at an arbitrary point O depends on the total energy E_o contributed by all the ions deposited within the range of the distribution. If shadowing effects and redeposition of the eroded material are ignored, the normal erosion velocity at O is given by

$$V_o = p \int_R dr \Phi(r) E(r) \quad (2-2)$$

where the integral is taken over the region R of all points at which the deposited energy contributes to E_o , $\Phi(r)$ is a local correction to the uniform flux J due to variation of the local slopes, and the material constant p depends on the surface binding energy and scattering cross-section (Sigmund, 1969 & 1973) as

$$p = \frac{3}{4\pi^2} \frac{1}{NU_o C_o} \quad (2-3)$$

where N is the density of target atoms, U_o is the surface binding energy and C_o is a constant proportional to the square of the effective radius of the inter-atomic interaction potential.

The erosion velocity is dependent on the curvature. When the ion beam is normally incident on a periodic disturbance, as shown in Figure 2.3, the energy deposited at the point O by ions striking the surface is the same as that deposited at O' by ions striking the surface there. However, the average energy deposited at O by an ion which hits the surface at A is greater than that deposited at O' by an ion incident at A' , and similarly for B and B' . Thus the rate of erosion at O is greater than that at O' , *i.e.*, the troughs are eroded more rapidly than the crests. Sputtering increases the amplitude of the perturbation and therefore leads to increase of surface roughness.

Figure 2.3 Schematic illustration of the physical origin of the instability during ion sputtering of non-planar surfaces.

In general, Sigmund's theory is in good agreement with many experimental results.

However, it has following two limitations:

- (1) The assumption of random slowing down and arbitrary collisions works satisfactorily only at intermediate and high energies, *i.e.* when $\varepsilon \sim 1\text{--}100$ keV, but may break down at low energies (Makeev *et al.*, 2002);
- (2) The assumption of a planar surface may influence the magnitude of the sputter yield, since surface roughness has a tendency to increase the yield (Makeev and Barabási, 1998a; Makeev and Barabási, 1998b).

2.3 Factors influencing the sputtering yield

The most important and most widely investigated quantity for describing the sputtering process is the sputtering yield Y , defined as the average number of atoms leaving the surface of a solid per incident ion (Behrisch and Wittmaack, 1991). Usually the number of sputtered atoms is orders of magnitude smaller than the total number of atoms participating in the collision cascade.

(1) The dependence of the sputtering yield on the surface binding energy:

Sputtering yield decreases as the chemical bond (such as metallic, covalent or ionic bond) strength of the milled material increases (Steckl and Chyr, 1999).

(2) The dependence of the sputtering yield on the energy of the impinging ion beam:

The study of Greene *et al.* (1997) revealed that the sputtering yield initially exhibited a quadratic dependence on the incident ion energy, and then approached a plateau at higher energies. At even higher energies the sputtering yield actually decreased since the incident ions penetrated the target much further and collisions with the target atoms occur too deep to return to the surface.

(3) The dependence of sputtering yield on the incidence angle:

The sputtering yield shows an increase with incidence angle and reaches a maximum between 70° and 80° (Prenitzer, 1999; Xu *et al.*, 1992). During the collision the incident

ion imparts to the target atom a velocity with a component in the outward direction from the surface in order for that atom to be sputtered. When the incidence angle approaches 90° , a higher percentage of the ions become backscattered and therefore do not participate in the sputtering of the target atoms. Another explanation (Smentkowski, 2000) is related with ion channeling at large incidence angles. For large sputtering angles, ions can travel (channel) through valleys in the atomic rows of the crystalline samples without hitting surface atoms. The energy deposited near the surface decreases substantially during channeling, reducing the sputtering yield.

(4) The dependence of sputtering yield on crystal orientation:

Crystal orientation also affects the sputtering yield. The sputtering yield was reduced when the ion beam was incident along more densely packed directions and enhanced for less densely packed directions (Onderdelinden, 1966; Smentkowski, 2000; Southern *et al.*, 1963).

2.4 Surface smoothing

The mechanism of surface microroughening proposed by Sigmund (1973) leads to instability of a plane surface against periodic disturbances. Counterbalancing the ion-induced roughening is the smoothing of surface due to effect of surface diffusion (Figure 2.4), as described by Herring and Mullins (Herring, 1950; Mullins, 1959). Diffusion, driven by surface energy minimization, occurs to smooth the surface morphology and is proportional to the divergence of the surface curvature,

$$\frac{\partial h}{\partial t} = -B \nabla^4 h \quad (2-4)$$

The constant B is given by

$$B = \frac{D_s C_{ss} \gamma}{n^2 k_B T} \quad (2-5)$$

where γ is the surface energy per unit area, D_s is the surface diffusion coefficient, C_{ss} is the concentration of the mobile species on the surface, n is the areal concentration of atomic sites. k_B is the Boltzmann's constant and T is the surface temperature.

Figure 2.4 Schematic illustration showing surface diffusion during ion sputtering.

There are two mechanisms contributing to surface diffusion: thermally induced surface diffusion and ion-induced smoothing. At high temperatures thermal surface diffusion is rather intensive, thus it is the main mechanism determining the relaxation process. In the absence of ion bombardment surface diffusion is thermally activated and characterized by the diffusion constant:

$$D_T = D_o \exp[-E_d / k_B T] \quad (2-6)$$

where D_0 is preexponential factor, E_d is the activation energy for surface diffusion of the adatoms and T is the substrate temperature.

The most common effect of ions on surface diffusion is related to direct transfer of the energy and momentum to the surface atoms by ion-atom collisions, changing the diffusion probability of an atom to diffuse from $P \sim \exp[-E_d/k_B T]$ to $P \sim \exp[-(E_d - E_i)/k_B T]$, where E_i is the energy transferred from the ion to the surface atom. MacLaren *et al.* (1992) bombarded GaAs with 17 keV Cs^+ ion and observed the development of ripple structure on the surface with a wavelength proportional to the square root of the diffusion constant for temperature ranging from 45 °C to 100 °C. When decreasing the temperature, the ripple spacing did not decrease exponentially to zero but stabilized at a constant value, providing direct evidence for a temperature independent ion-induced surface diffusion constant.

It has been demonstrated that a large number of adatoms are created on a surface during ion sputtering by Teichert *et al.* (1994), who noted that these adatoms nucleate in monatomic height islands, indicating that they diffuse significantly on the surface and contribute to the final surface morphology.

Makeev and Barabási (1997) demonstrated the existence of a new mechanism for ion-induced diffusion, showing that sputtering can lead to preferential erosion that appears as surface diffusion, even though no actual mass transport along the surface takes place in the system. They calculated the ion-induced effective surface diffusion

constant and its dependence on the ion energy, flux and angle of incidence, showing that sputtering can both enhance and suppress surface diffusion.

2.5 Bradley and Harper model of ion-sputtered ripple formation

Ripples have been observed on surfaces of a wide variety of materials after they are irradiated with ions at an off-normal angle. The first explanation of this phenomenon is proposed by Bradley and Harper (1988). The well-accepted Bradley-Harper model (BH model) is a linear analysis of a surface undergoing the competition between roughening due to sputtering and smoothing due to annealing by thermal diffusion. Based on the Sigmund theory of isotropic collision cascades, the approach relates the sputter yield to the energy deposited onto the surface by the incoming ions. The work by Bradley and Harper (1988) has demonstrated for the first time that the yield variation with the local surface curvature induces an instability, which leads to the formation of periodically modulated surface structures. This instability is caused by the different erosion rates for troughs and crests, the former eroded faster than the latter (Figure 2.3). Combining the curvature dependent erosion velocity with the surface smoothing mechanism due to surface diffusion (Herring, 1950; Mullins, 1959), BH derived a linear equation for surface morphology evolution,

$$\frac{\partial h}{\partial t} = -V(\theta) + v_x(\theta)\partial_x^2 h + v_y(\theta)\partial_y^2 h - K\nabla^4 h \quad (2-7)$$

where $V(\theta)$ is the erosion rate, $v_x(\theta)$ and $v_y(\theta)$ are the effective surface tensions generated by the erosion process, dependent on the angle of incidence of the ions, θ , K

is the relaxation rate due to surface diffusion:

$$K = (D_s \gamma \Omega^2 n / k_B T) \exp\{-\Delta E / k_B T\} \quad (2-8)$$

where ΔE is the activation energy for surface diffusion, γ is the surface energy per unit area, $k_B T$ is thermal energy, D_s is the surface diffusion coefficient, Ω is the atomic volume and n is the number of molecules per unit area on the surface.

The physical instability, as illustrated in Figure 2.3, leads to the negative signs of the v_x , v_y coefficients in Equation (2-7). Equation (2-7) is linearly unstable, with a Fourier mode k_c whose amplitude exponentially dominates all the others. This mode is observed as the periodic ripple structure. Using linear analysis, BH derived from Equation (2-7) the ripple wavelength as:

$$\ell_c = 2\pi/k_c = 2\pi \sqrt{\frac{2K}{|v|}} \sim (JT)^{-1/2} \exp\left\{\frac{-\Delta E}{k_B T}\right\} \quad (2-9)$$

where v is the largest in absolute value of the two negative surface tension coefficients v_x and v_y , and J is the ion flux.

The calculation also predicts that the ripple direction is a function of the angle of incidence: For large θ the ripples are parallel to the surface component of ion beam direction, while for small θ they are perpendicular to it as illustrated in Figure 2.5.

Figure 2.5 Dependence of the ripple orientation on the angle of incidence θ : (a) orientation for small θ and (b) orientation for θ close to $\pi/2$. (Bradley and Harper, 1988)

The BH model is rather successful in predicting the ripple wavelength and orientation in agreement with many experimental observations. However, it cannot account for ripple orientations that are neither parallel nor perpendicular to the projected ion direction. Experiments on metals (Costantini *et al.*, 2001; Ondrejcek *et al.*, 2003; Rusponi *et al.*, 1998a) demonstrate that the surface crystallography can play an important role in the ripple formation. Ripple can form even at normal incidence angle (Costantini *et al.*,

2001). The substrate temperature can be used to select and enhance only certain diffusion processes and consequently tune the final surface morphology (Rusponi *et al.*, 1998a). For grazing incidence ion bombardment of metal substrates, the ripples grow along the projected ion beam direction and do not depend on the crystallographic orientations (Chan *et al.*, 2004). The roughness and wavelength follow a power law with dose (time) (Chason and Aziz, 2003).

In addition, the BH model is linear, predicting unbounded exponential growth of the ripple amplitude, thus it cannot account for the stabilization of the ripples as observed by Erlebacher *et al.* (2000). Another problem with the BH model is that it cannot account for low temperature ripple formation since the only smoothing mechanism it considers is of thermal origin. Despite these shortcomings, the BH theory represents a major step in understanding the mechanism of surface pattern evolution during ion sputtering.

Several modifications (Cuerno and Barabási, 1995; Valbusa *et al.*, 2002) to the model have been proposed that enable it to be extended to the non-linear regime, such as the satisfactory explanation of amplitude saturation, as described in the following Section.

2.6 Nonlinear theory on ripple formation

Since the linear BH model (1988) fails to explain a number of experimental features, such as the saturation of the ripple amplitude, or the appearance of kinetic roughening. It has been proposed that these shortcomings can be cured by the inclusion of nonlinear

terms and noise.

Cuerno and Barabási (1995) derived a stochastic nonlinear continuum equation, called the Kuramoto-Sivashinsky (KS) equation, to describe the morphological evolution of amorphous surfaces eroded by ion bombardment. Consequently Equation (2-7) has to be replaced by the nonlinear equation:

$$\partial_t h = v_x \partial_x^2 h + v_y \partial_y^2 h - D_x \partial_x^4 h - D_y \partial_y^4 h - D_{xy} \partial_x^2 \partial_y^2 h + \frac{\lambda_x}{2} (\partial_x h)^2 + \frac{\lambda_y}{2} (\partial_y h)^2 + \eta(x, y, t) \quad (2-10)$$

where λ_x and λ_y describe the tilt-dependent erosion rate, depending on flux J and the penetration depth a , and $\eta(x, y, t)$ is a Gaussian white noise with zero mean and variance proportional to the ion flux, accounting for the stochastic arrival of ions to the surface (Cuerno and Barabási, 1995). Furthermore, the sputtering process always generates ion induced effective diffusion (Makeev and Barabási, 1997) that, together with thermal diffusion (Bradley and Harper, 1988), is incorporated in D_x , D_y , and D_{xy} .

Under normal incidence angle, the coefficients in Equation (2-10) are isotropic (Kahng *et al.*, 2001; Makeev and Barabási, 1997):

$$v \equiv v_x = v_y = -faa_\sigma^2 / 2a_\mu^2 \quad (2-11)$$

$$D \equiv D_x = D_y = fa^3 a_\sigma^2 / 8a_\mu^4 \quad (2-12)$$

$$\lambda \equiv \lambda_x = \lambda_y = (f/2a_\mu^2)(a_\sigma^2 - a_\sigma^4 - a_\mu^2) \quad (2-13)$$

where $a_\mu = a/\mu$, $a_\sigma = a/\sigma$, μ and σ are the width of energy distribution in directions

perpendicular to and parallel to the incoming ions respectively (Figure 2.2).

In the $\lambda > 0$ case, at the early stages of the sputtering process the surface is dominated by small, wavy perturbations generated by the interplay between the ion induced instability and surface relaxation. However, since the system is isotropic in the (x,y) plane, these ripple precursors are oriented randomly, generating short wormlike morphologies on the surface. After some characteristic time, τ , these structures turn into isolated but closely packed islands, reminiscent of the quantum dots (QDs) reported experimentally (Bobek *et al.*, 2001; Chen *et al.*, 2002; Facsko *et al.*, 1999). As the sputtering proceeds, the supporting surface develops a rough profile, destroying the overall uniformity of the islands.

A similar scenario is observed for $\lambda < 0$, the only difference being that now the islands are replaced by holes. Thus the development of QDs and holes is governed by the same underlying physical phenomena, the only difference being that for QDs $\lambda > 0$, and for holes $\lambda < 0$.

According to Equation (2-13) the sign of λ is determined only by the relative magnitude of a_σ and a_μ ; therefore, whether islands or holes appear is determined by the shape of the collision cascade. These results also indicate that the QDs and holes are inherently nonlinear objects, since if the linear terms should be responsible for their formation, the surface morphology should not depend on the sign of λ (Kahng *et al.*,

2001).

Facsko *et al.* (Bobek *et al.*, 2001; Facsko *et al.*, 1999) investigating low-energy normal incident Ar^+ ion sputtering of GaSb (100) surfaces, observed that as erosion proceeds, nanoscale islands appear on the surface, that are remarkably well ordered, and have a uniform size distribution as shown in Figure 2.6.

Figure 2.6 (a) AFM-height profile of quantum dot structures created on GaSb with ions of 500 eV energy and (b) autocorrelation of (a). (Facsko *et al.*, 1999)

Numerical simulations (Park *et al.*, 1999) have shown that there is a clear separation of the linear and nonlinear regimes in time: For short erosion times, the ripple development and orientation follow the predictions of the linear theory of BH (Bradley and Harper, 1988). However, after a well-defined crossover time, which depends on the relative

signs of v_x , v_y , λ_x and λ_y , the surface morphology is determined by the nonlinear terms. Kinetic parameters such as surface diffusion and flux are important in determining the ripple wavelength and the rate at which it grows, but the qualitative behaviour of which type of ripples form and whether they are stable are determined by geometric effects due to the incidence angle and the collision cascade. Makeev *et al.* (2002) have summarized the different morphological regime in a phase diagram as shown in Figure 2.7. Regions in Figure 2.7 are discussed separately as follows:

Region I: v_x , v_y , λ_x and λ_y are all negative. At short time scales, the linear theory predicts ripple oriented along the x or y direction depending on the relative magnitude of v_x and v_y . At long times, the nonlinear terms begin to take over, the ripple structure disappears and the surface undergoes kinetic roughening.

Figure 2.7 Phase diagram of the dependence of ripple formation on a_σ and incidence angle θ for the symmetric case ($\sigma = \mu$). Region I: $v_x < 0$, $v_y < 0$, $\lambda_x < 0$, $\lambda_y < 0$; Region II: $v_x < 0$, $v_y < 0$, $\lambda_x > 0$, $\lambda_y < 0$; Region III: $v_x > 0$, $v_y < 0$, $\lambda_x > 0$, $\lambda_y < 0$. (Makeev *et al.*, 2002)

Region II: Compared with Region I, $\lambda_x \lambda_y$ is negative. Studies by Park *et al.* (1999) have shown that three morphological regimes can be distinguished with time evolution. For short times, the ripple structure predicted by the linear theory is observed. Ripple is orientated along the direction which has the largest value of v . For intermediate times, the surface is rough. If this roughness would follow kinetic roughening, one would expect logarithmic scaling. However, this transient regime is somewhat different from

what is expected during kinetic roughening. The numerical simulations often show the development of individual ripples, which soon disappear without long-range order. However for long time, a new ripple structures suddenly forms. Such ripples are stable and the orientation θ_c is rotated with respect to the x direction. The angle θ_c , calculated by Rost and Krug (1995), has the value $\theta_c = \tan^{-1} \sqrt{-\lambda_x/\lambda_y}$.

Region III: This region is characterized by a positive v_x and a negative v_y . At short time scales, the ripple structures are formed with orientation along the y direction. The long-time behavior is complicated but analysis suggests that a rotated ripple morphology will develop similar to Region II.

Rotated ripple structure (RRS) was first predicted by Rost and Krug (1995), and then simulated numerically by Park *et al.* (1999). Kim *et al.* (2002) investigated the necessary conditions for the formation of RRSs and the impact of the various experimentally controllable parameters on the morphology of the RRS. They found that at low temperatures the RRSs could form when the longitudinal width (σ) of the damage cascade generated by the ion beam was larger than the transverse width (μ). By calculating the structure factor for the RRS, they also found that RRS were more regular and their amplitude was more enhanced compared to the much studied ripple structure forming in the linear regime of sputter erosion. The experimental result for graphite surface (Habenicht *et al.*, 2000) shows that σ depends on ϵ , while μ is independent of ϵ for large ϵ (2-50 keV), $\sigma > \epsilon$ condition could be met when the energy of the incident ion beam is high enough. Besides the condition $\sigma > \epsilon$, the incident angle has to be chosen

appropriately. The window of such angles is rather narrow (Figure 2.8). While the presence of the RRS was proposed theoretically, the structure has not been observed experimentally yet.

Figure 2.8 The shaded region in the parameter space (θ , a_σ) for $a_\sigma=1$ (inset: for $a_\sigma=2$) corresponds to the region where the RRS can form. (Kim *et al.*, 2002)

Understanding of sputtering from rough surfaces is far from complete. Major analytic results have been obtained without accounting for sputtering anisotropy, diffusion anisotropy and overlooking shadowing of particles and redeposition (Carter, 1999; Makeev and Barabási, 1998a; Makeev and Barabási, 1998b; Stepanova *et al.*, 2002).

2.7 Experimental observation

2.7.1 Ripple amplitude

According to the linear BH model (1988), the ripple amplitude should grow exponentially with time. The nonlinear theory developed by Cuerno and Barabási (1995) supplements the BH model and predicts that the ripple amplitude will stabilize after initial growth. This is consistent with the experimental observations (Erlebacher *et al.*, 1999). Erlebacher *et al.* (1999) studied the evolution of the ripple amplitude on sputtered Si (0 0 1) surfaces in real time by means of light scattering. The data in Figure 2.9 show measurements of the ripple amplitude made at various ripple wavelengths and surface temperatures. At initial stages the ripple amplitude is growing exponentially. However the exponential growth stops at some time and the ripple amplitude saturates.

Figure 2.9 Non-linear evolution of ripple amplitude on Si surfaces measured by light scattering. (Erlebacher *et al.*, 1999)

2.7.2 Ripple orientation

An important feature as predicted by the BH model, the linear theory, is the ripple orientation depending on the incidence angle. The earliest observed ripples on glass by Navez *et al.* (1962) are of the BH-type, as shown in Figure 2.10. The glass surface was irradiated with broad ion beam for 6 hours at incidence angles ranging from 30° to 80°. For incident angles close to $\theta = 0^\circ$ (Figure 2.10(b)), the ripples are perpendicular to the ion beam direction, while they are parallel to the ion beam direction when the beam reaches the surface at grazing incidence (Figure 2.10(d)). In contrast, when the ion bombardment is performed at exactly normal incidence (Figure 2.10(c)), no long-order

periodic structures are observed.

The nonlinear theory also predicts that new ripple with orientation different from both x and y directions might appear. Such rotated ripples have never been observed in practice till now.

Figure 2.10 Experiment of Navez *et al.* on glass. (a) An Azam ion gun working with an acceleration voltage of 4 kV, an ion beam with an angular divergence $< 10^\circ$ and a flux ranging from 0.5 to $2 \mu\text{A}\cdot\text{mm}^{-2}$. (b) $\theta = 30^\circ$. (c) $\theta = 0^\circ$, (d) $\theta = 80^\circ$. The arrow indicates the projected ion beam direction. (Navez *et al.*, 1962)

2.7.3 Ripple formation on metals

The theory mentioned above is sufficient to explain many measurements on semiconductor and amorphous materials, in which the ripple orientation is determined by ion beam direction and not influenced by crystallographic orientation. However, experiments carried out on metals such as Cu, Ag, Pt and Au under similar experimental conditions (ion energy 1-5 keV and ion flux 4-50 $\mu\text{A}/\text{cm}^2$) show that surface crystallography can play an important role in pattern formation.

Ion sputtering at normal incidence produces well defined periodic features that reflect the symmetry of the substrate without any relation with the ion beam direction: square pits on Cu (001) (Ritter *et al.*, 1996) and Ag (001) (Costantini *et al.*, 1998), hexagonal ones on Pt (111) (Michely and Comsa, 1993), Au (111) (Murty *et al.*, 1998) and Cu (111) (Naumann *et al.*, 1997).

For anisotropic substrates, such as Ag (110) (Costantini *et al.*, 2001; Rusponi *et al.*, 1997) and Cu (110) (Rusponi *et al.*, 1998a) surfaces, ripple appears after sputtering at normal incidence angle. However ripple formation is related with substrate temperature. No ripples are present on the Ag (110) and Cu (110) surfaces irradiated with normal angle at low temperature (180 K) (Figure 2.11(a)). In contrast, ripples are observed for higher substrate temperatures such as 230 K (Figure 2.11(b)), 300K (Figure 2.11(d)) and 320 K (Figure 2.11(e)) on Ag (110). The orientation of ripple structures produced on Cu (110) (Rusponi *et al.*, 1998a) and Ag (110) (Costantini *et al.*, 2001) at normal sputtering can be

tuned from $\langle 001 \rangle$ to $\langle 1\bar{1}0 \rangle$ by increasing the substrate temperature (Figure 2.11) or decreasing the ion flux (Figure 2.12). Off-normal sputtering at low temperature (180 K) (Valbusa *et al.*, 2002) generates ripples whose orientation depends on both ion direction and surface azimuthal orientation.

The roughness and wavelength (Murty *et al.*, 1998; Rusponi *et al.*, 1998b) on irradiated metal surfaces follow a power law with dose (time), very similar to those measured on substrate with an Ehrlich-Schwoebel barrier (Ehrlich and Hudda, 1966; Schwoebel and Shipsey, 1968) at the step edges. Rusponi *et al.* (1998a) proposed a diffusion-based roughening mechanism originating from the presence of Ehrlich-Schwoebel barriers, adapted from a model proposed by Villain *et al.* (Politi and Villain, 1996; Villain, 1991) for the morphology of crystal growth. In the model by Villain *et al.* supersaturated adatoms (either from growth or sputtering) on a high symmetry surface prefer to stick to the edge of the upper terraces rather than the lower ones because of the Ehrlich-Schwoebel barrier. This results in a net uphill adatom current that induces surface roughening.

The strength of diffusion-based roughening mechanism depends on both the fraction of adatoms that attach to the step edge and the degree of biasing in attachment. Since at high temperature the steps are less effective sinks for adatom and the degree of biasing is less, the roughening mechanism due to Ehrlich-Schwoebel barrier is expected to decrease at higher temperature. This barrier is expected only to be reasonably large in fcc metals and could be expected to be influential in controlling morphology evolution on these

materials at not too high temperatures (Carter, 2001).

Figure 2.11 STM images (size $400 \times 400 \text{ nm}^2$) of Ag (110) after ion sputtering at normal incidence for different temperature T_s . (a) 180 K; (b) 230 K; (c) 280 K; (d) 300 K; (e) 320 K; (f) 350 K. (Costantini *et al.*, 2001)

Figure 2.12 STM images (size $400 \times 400 \text{ nm}^2$) showing Ag(110) surface morphology after ion sputtering with normal incidence at $T_s=300 \text{ K}$ and $t=20 \text{ min}$. The ion flux Φ is: (a) $\Phi=4 \text{ } \mu\text{A}/\text{cm}^2$; (b) $\Phi=10 \text{ } \mu\text{A}/\text{cm}^2$; (c) $\Phi=16 \text{ } \mu\text{A}/\text{cm}^2$; (d) $\Phi=29 \text{ } \mu\text{A}/\text{cm}^2$. The insets show 2D-autocorrelation. (Costantini *et al.*, 2001)

The nonlinear theory proposed by Cuerno and Barabási (1995) describes only an isotropic diffusion on a flat surface. It does not take into account that the adatom (or vacancy) mobility on a single crystal metal surface is actually biased both in the vertical direction, by an Ehrlich-Schwoebel barrier at the step edges, and in the surface plane, by a diffusion rate which is different along different crystallographic orientations. To better explain experimental results on ion sputtered metal surface, Rusponi *et al.* (1998a)

proposed to include the crystal anisotropy and Ehrlich-Schwoebel barrier in the diffusive term of Equation (2-10).

2.8 Broad ion beam vs. focused ion beam

Most experiments mentioned above were carried out with broad ion beam at low ion energy. Ion/solid interactions have been investigated for broad ion beam irradiation to a great extent. Compared with broad ion beam, focused ion beam has much higher current density ($> 1\text{A}/\text{cm}^2$) and much smaller beam size ($< 50\text{ nm}$). Certain aspects of the interactions must be unique to focused ion beam bombardment. Experiment on Si by Cuenat and Aziz (2002) seems to be the first one which compared the spontaneous pattern formation with focused and unfocused ion beam irradiation. They found that the ripples appeared to be more regular when produced with the FIB than with the unfocused Ar^+ beam (Figure 2.13). The authors also found that the boundary of FIB-irradiated region changed the pattern formed in its vicinity. Differences in beam characteristics or pattern formation mechanisms warrant further research.

Figure 2.13 (a) Sputter-induced ripples on Si (001) after bombardment with an unfocused 750 eV Ar^+ beam at 600 °C. Wavelength = 520 nm. (b) Sputter-induced ripples on Si (001) after bombardment with a focused 30 keV Ga^+ beam at room temperature. Wavelength = 2.15 μm. (Cuenat and Aziz, 2002)

2.9 Modelling of sputtering process

The sputtering process and collision cascade can be described using Monte Carlo (MC) simulation. MC simulation method relies on the statistical or random nature of the process modeled. The movement of an ion in the solid is handled as series of binary collisions of atoms. The scattering is calculated using an inter-atomic potential and the conservation laws of the momentum and energy of the particles. Two major forms of energy loss are included in the slowing down process of energetic ions in the target. They are interaction of ions with the electrons in the solid, which is usually referred to as the inelastic energy transfer process, and collisions of ions with the nuclei of the target, which is usually referred to as the elastic energy transfer process.

SRIM (the stopping and range of ions in matter), a Monte Carlo computer program, was developed by Biersack and Haggmark (1980) and Ziegler *et al.* (1985), which calculates the ion range and damage distributions of the backscattered and transmitted ions in amorphous target. The used SRIM code in this study originates from the software package SRIM-2003 available online from the Internet. The inputs for simulation includes ion element, ion energy, incidence angle, target material and total number of ions. SRIM can generate data regarding the final 3D distributions of ions, as well as all kinetic data associated with the energy loss of the ion to the solid (Giannuzzi and Stevie, 2005). For example, target damage, average sputtering yield per incident ion, ionization, and phonon production can all be quantitatively modeled using SRIM.

Two key quantities that describe spatial distribution of the energetic ions inside the amorphous solid, projected range (R_p) and projected range straggling (ΔR_p), can be calculated using SRIM, which takes into account the nuclear and electronic stopping as independent processes. The total distance that the ion travels in solid target is called the range. The projection of this distance onto the direction of incidence is called the projected range. Because both the number of collisions and the energy transferred per collision are random variables, all the ions of a given surface and initial energy will not be the same range. There will be a distribution of stopping points in space, or a range distribution, which must be characterized by quoting a mean ion range, a standard deviation in the ion range. When projected onto the incident direction, these are referred to as the projected range (R_p) and projected range straggling (ΔR_p) (Chen, 1994). R_p is the depth at which the highest concentration of implanted ions will be found.

It should be noted that SRIM treats all targets as amorphous, thereby discarding the potential contribution of orientation dependent phenomena to range distributions (Giannuzzi and Stevie, 2005). This should be considered when attempting to simulate damage cascades during FIB milling of crystalline materials.

2.10 Summary

This chapter reviewed ion sputtering mechanisms and models on formation of ion-induced surface patterns. The competition between thermal diffusion and the curvature-dependent instability causes the formation of periodic surface structures, as predicted by linear BH model. The nonlinear theory is developed by introducing nonlinear terms and noise into BH model. For short time scales, the linear model can well predicts ripple formation. While at long time scales the nonlinear terms dominate the evolution of the surface morphology. The nonlinear terms lead to the stabilization of the ripple amplitude and the formation of rotated ripple structures. Anisotropic surface diffusion and Ehrlich-Schwoebel barrier are introduced to account for ripple formation both at normal and off-normal incidence angles and the scaling law of ripple growth.

Most experiments in the past were carried out using broad ion beam and the theories developed all assume broad ion beam. The difference between broad ion beam and focused ion beam requires distinct consideration to develop new models describing new phenomena that may be particular to focused ion beam irradiation.

Chapter 3 Experimental Procedures

3.1 Introduction

This chapter is written to describe FIB technology, sample preparation methods and various characterization techniques used in the project. The field of focused ion beam (FIB) has advanced rapidly since the application of the first liquid metal ion sources (LMIS) in the 1970s. The development of LMIS, a key component of ion column, has resulted in a powerful tool for both research and industry (Orloff *et al.*, 2002). The development of LMIS is first reviewed (Section 3.2.1). Then lens system for focusing, deflecting and scanning is introduced (Section 3.2.2). Section 3.2.3 discusses experimental variables related with ion milling and summarized specifications and capabilities of FIB machines used in the project. Since there is secondary particle emission upon ion bombardment, FIB can also be used as a tool for imaging (Section 3.2.4). Introduction to FIB technique (Section 3.2) is followed by sample preparation methods (Section 3.3) and instruments for characterizing the FIB irradiated surfaces (Section 3.4).

3.2 Focused ion beam technique

3.2.1 Liquid metal ion source

The work on electrohydrodynamic spraying of liquids played an important role in the development of liquid metals as a source of positive ions. Bose first reported the phenomenon when he observed the formation of water threads at the nozzle of an electrified capillary (Prewett and Mair, 1991). Lord Rayleigh made the first calculations on the effects of electric stress on conducting fluids (Prewett and Mair, 1991). Since then, researchers had performed various experiments involving liquids such as water, ethyl alcohol, glycerine, soap bubbles and various atmospheres such as air, hydrogen and carbonic acid. It was Taylor who, in his classic paper, showed theoretically that an uncharged spheroid droplet could exist in equilibrium in a uniform electric field provided (Prewett and Mair, 1991):

$$F(r_0/\gamma)^{1/2} < 1.625 \quad (3-1)$$

where F is a uniform electric field (Vcm^{-1}), γ is the surface tension (dyn/cm) and r_0 is the radius of the droplet (cm).

The first liquid metal ion source (LMIS) was developed in 1975 (Krohn and Ringo, 1975). The ion source had a brightness of $0.9 \times 10^5 \text{ Acm}^{-2}\text{sr}^{-1}$ at 21 kV and the effective source diameter of 0.2 μm . Four years later Seliger *et al.* (1979) managed to produce a Ga^+ FIB with a diameter of only 100 nm and a current density of 1.5 Acm^{-2} and brightness of $3.3 \times 10^6 \text{ Acm}^{-2}\text{sr}^{-1}$ at 57 kV. In the following years, significant progress

has been made in FIB technologies. Presently there are many kinds of LMISs (Latif, 2000) including Au, Cs, In, Bi, Pb, Ga, *etc.*, however Ga^+ ion source is currently the most commonly used due to its low melting point ($\sim 30^\circ\text{C}$), low vapor pressure, very high brightness ($10^6 \text{ Acm}^{-2}\text{sr}^{-1}$), long lift time (~ 1500 hours) and high stability.

A Ga liquid-metal ion source (LMIS) is schematically shown in Figure 3.1. A reservoir of gallium (Ga) is positioned in contact with a sharp tungsten (W) needle. The Ga liquefies upon heating and flows to the W tip. An equilibrium conical shape known as the Taylor cone forms due to the competition between the electrical force and the surface tension. The radius of the apex of the Taylor cone depends on the radius of the W needle and the emission current and is within the range of 2-10 nm (Giannuzzi and Stevie, 1999; Latif, 2000). The Ga^+ ions are emitted from the sharp point of the Taylor cone by a high extraction voltage.

Figure 3.1 Schematic diagram of LMIS structure.

3.2.2 Lens system

Figure 3.2 shows a schematic diagram of the FIB system. After a first refinement through the acceptance aperture, the ion beam is condensed in the first electrostatic lens. The upper octupole then adjusts the beam stigmatism. Using the variable aperture mechanism, the beam current can be varied, allowing both a fine beam for high-resolution imaging on sensitive samples and a heavy beam for fast and rough milling (Reyntjens and Puers, 2001). Blanking of the beam is accomplished by the deflector plate and blanking aperture, while the lower octupole is used for raster scanning the beam over the sample in a user-defined pattern. In the second electrostatic lens, the beam is focused to a fine spot, enabling a best resolution in the sub 10 nm range. The multichannel plate (MCP) is used to collect secondary particles for imaging. The imaging principle is discussed in the Section 3.2.4.

Figure 3.2 Schematic diagram of focused ion beam system.

3.2.3 Milling

Ion milling is one of the most important functions of the FIB. During ion milling the beam is unblanked. Lines, circles, rectangles and stepped profiles can be milled using the scan control system.

There are two scan styles of focused ion beam, as shown in Figure 3.3. In raster scan, the beam proceeds along each scan line, always in the same direction. At the end of each scan line, the beam is blanked and repositioned to the start of the next scan line. After the last scan line in the raster, the beam is blanked and repositioned to the start of

the first scan line. Scanning continues until the specified dose is delivered. While for serpentine scan, scanning direction is reversed at the end of each scan line (Micrion, 1997). Raster scan was used throughout the project.

Figure 3.3 Scan styles of focused ion beam spot: (a) raster scan; (b) serpentine scan.

Beam spot moving from one position to the next forms beam overlap. There are beam overlaps in both x and y directions. The calculation of overlap is illustrated in Figure 3.4. Dwell time is the period of time the beam stays at a particular position. Both dwell time and overlap are important parameters used in FIB milling since they affect collision cascade. Chapters 4 and 6 show new knowledge gained through the project regarding the effect of these two parameters on sputtering yield and surface patterning. If not specified in the context, the default overlap and dwell time were 50% and 3 μs , respectively.

Figure 3.4 Schematic of beam overlap. D represents the distance between adjacent beam spots, while r indicate the radius of spot. The spot overlap is calculated as $|2r - D|/2r$.

Material, ion dose, ion current, incidence angle, dwell time, beam overlap, and crystallographic orientation were varied to investigate their effects on pattern formation at room temperature. Effect of irradiation temperature was not studied because of difficulty in incorporating heating and cooling stage. Experimental geometry is illustrated in Figure 3.5. θ represents incidence angle and β indicates surface azimuthal orientation. Introducing of azimuthal angle is convenient for studying the relationship between the ripple direction and crystallographic orientation.

Major manufacturers that produce FIB instruments include FAI, FEI, Hitachi, JEOL, Seiko and NANOFAB *et al.* (Giannuzzi and Stevie, 1999; Prenitzer, 1999). There are two types of FIB systems used in the project. One is Micrion (it is now a part of FEI) 9500EX FIB/SEM dual beam system, as shown in Figure 3.6(a). The other is FEI Quanta 3D 200 FIB/SEM dual beam system, as shown in Figure 3.6(b). Both of the systems are equipped with liquid gallium ion sources.

Figure 3.5 The experimental geometry. (x, y, z) represents the laboratory frame, h is normal to the flat surface, while ion trajectories are assumed to lie in the x - z plane. θ is ion incidence angle and β represents surface azimuthal orientation.

Figure 3.6 Photos of FIB/SEM dual beam systems used in the project: (a) Micrion 9500EX; (b) FEI Quanta 3D 200.

For the Micrion FIB system, the ion beam energy can be adjusted between 5 and 50 keV, with beam currents varying between 4 pA and 20 nA. The minimum spot size is 7

nm in diameter. Pressure in the work chamber is typically maintained in the order of 10^{-7} torr. FIB current of 1 nA with nominal spot size of 60 nm at 30 kV was used in the experiments carried out using the Micrion FIB.

Most of the experimental work is carried out using Quanta FIB. The maximum ion energy for Quanta FIB is 30 keV and the best resolution is 10 nm. Focused ion beam intensity resembles a Gaussian distribution. The intensity at the tail of the beam is not strong enough to sputter materials and negligible. The full width at half-maximum (FWHM) is commonly used to describe the beam diameter (Tseng, 2004). Beam parameters for 30 keV Ga^+ ions at a 30 mm working distance are listed in Table 3.1. Ion beam diameter as a function of beam current for the Quanta system is shown in Figure 3.7. Current density as a function of ion beam current is shown in Figure 3.8. Current density achieves the maximum value at ion current of 3 nA (Figure 3.8).

Table 3.1 Beam parameters for 30 keV Ga^+ ions at a 30 mm working distance (Quanta FIB) (FEI company, 2004).

Beam current (pA)	Beam diameter (nm)	Current density (A/cm ²)
1	7	2.60
30	16	14.93
50	19	17.64
100	23	24.08
300	33	35.09
500	39	41.88
1000	50	50.96
3000	81	58.25
5000	110	52.64
7000	141	44.85
20000	427	13.97

Figure 3.7 Ion beam diameter vs. beam current for the Quanta FIB system (FEI company, 2004).

Figure 3.8 Current density vs. ion beam current for the Quanta FIB system (FEI company, 2004).

3.2.4 Imaging

In addition to ion milling, FIB can also be used as an imaging instrument. A FIB instrument looks and operates much like a scanning electron microscopy (SEM) (Goldstein *et al.*, 2003). Both instruments rely on a focused beam to create a specimen image; an ion beam for the FIB and an electron beam for the SEM. For both instruments, the intensity of the secondary electrons produced at each raster position of the beam is displayed to create an image of the sample. In the FIB, secondary ions may also be detected and used to construct an image of the sample.

As illustrated in Figure 3.9, during FIB imaging the finely focused ion beam is raster scanned over a substrate, secondary particles (neutral atoms, ions and electrons) are ejected from the sample surface. A detector referred to as the MCP (microchannel plate) in the Micrion FIB system mounted near the bottom of the ion column, attracts and captures the secondary particles emitted by the sample. The detector bias is a positive or a negative voltage, respectively, for collecting secondary electrons or secondary ions. Everhart-Thornley Detector is used in FEI FIB system for secondary electrons detection.

Variations in surface topography and composition that are encountered as the ion beam scans the sample surface produce variations in the rate of secondary particle emission. The software in the FIB system then saves the secondary particle intensities as a function of the beam position and processes the output to the form of an image to the

display device. Secondary electrons are generated in much greater quantities than secondary ions (Orloff, 1997) and provide images of better quality and resolution; consequently the secondary electron mode is used for most imaging applications.

Figure 3.9 Schematic diagram showing secondary particle emission during ion beam sputtering.

Images generated by FIB are different from the images formed by SEM, this occurs due to the larger size of ions relative to the electrons, and due to the positive charge of ions. As the Ga^+ ions are much larger than electrons the interaction volume in FIB is lower than that in SEM; hence secondary electrons and secondary ions are generated from regions much closer to the specimen surface (Latif, 2000).

3.3 Materials and preparation of metallographically polished sample

Materials used in the experiments were pure tin (purity > 99.99%), commercially pure titanium (CP Ti), single-side-polished Si (100), InP (100), GaAs (100), and ZnO thin film on Si substrate. The former two metals need to be metallographically polished. The bulk materials (Sn & Ti) were first cut into small pieces of around $10 \times 10 \times 4 \text{ mm}^3$ in size. These small pieces of specimens were then cold mounted with room-temperature curing resin. The cured specimens were ground with silicon carbide paper of grits 180 manually to expose the specimen. This was to minimize the alteration of the sample structure that might be induced due to the deformation or local tempering generated during sawing process.

After removal of the mass material, the specimens (Sn & Ti) were ground with progressively finer silicon carbide paper (400 to 1200 grits). Careful cleaning of the specimens was performed between the steps to prevent cross contamination of coarse abrasive particles in the finer steps. In addition, grinding was performed with a rotation of the specimen by 90° after each step to eliminate scratches formed in the previous step.

After the fine grinding process, the specimens were polished with $3 \text{ }\mu\text{m}$, $1 \text{ }\mu\text{m}$ and $0.3 \text{ }\mu\text{m}$ diamond suspension sequentially at a constant rotating speed of 150 rpm. Polishing lubricant was applied frequently to avoid embedding of diamond particles into the sample surface. The specimens were held flat against the abrasive surface at all times to

obtain parallel and flat surfaces. Once metallographically polished specimens were ready, they were used for irradiation under focused ion beam.

3.4 Characterization techniques

3.4.1 Focused ion beam imaging

Some of specimens irradiated with focused ion beam were observed *in situ* using FIB imaging. The principle of FIB imaging is discussed in Section 3.2.4 in detail. Since the sputtering yield of secondary electrons is much higher than that of secondary ions during FIB scanning, secondary electrons were collected to construct better images in the project. To minimize material sputtering, small current (around 30 pA) was used for imaging.

3.4.2 Optical microscope

After specimens were irradiated with FIB, the surfaces were observed under ZEISS optical microscope. Due to good optical contrast, surface details of fine structures were sometimes detected although they might be beyond the resolution limit of optical microscope. Optical microscopy is a convenient and easy tool to capture surface image and provide quick feedback for planning further experiments. Image Pro Plus software was used to add the microbar and carry out quantitative measurements of area and length.

3.4.3 Scanning electron microscope (SEM)

Most SEM images were taken with the Quanta FIB/SEM dual beam system. However, a JEOL JSM LV5600 SEM and a LEICA S360 SEM (Cambridge, UK) was also used for other purposes, e.g., backscattered electron imaging and energy dispersive x-ray (EDX) analyses.

Although secondary electron images are obtained most frequently with the SEM, backscattered electron images also provide important information. Backscattered electrons vary in their amount and direction with the composition, surface topography, crystallinity and magnetism of the specimen. The backscattered electron image contains two types of information: one on specimen composition and the other on specimen topography. In composition images of crystalline specimens, the difference in crystal orientation can be obtained by utilizing the advantage that the backscattered electron intensity changes largely before and after Bragg's condition.

The pure Sn and CP Ti used in the project were polycrystalline. Backscattered electron images provided useful information to differentiate grains with different crystallographic orientations. JEOL SEM equipped with backscattered electron detector served this purpose.

The chemical composition after FIB irradiation was analysed using EDX integrated in LEICA SEM. EDX spectra were collected at various electron voltages ranging from 5

to 20 keV. It was found that smaller electron voltage induced smaller excitation volume and was more suitable for studying surface chemical composition, as presented in Chapter 8.

3.4.4 Atomic force microscope (AFM)

Atomic force microscope is a powerful tool in detecting the three dimensional topography in a digital format. Dimension 3000 AFM from Digital Instruments was used to characterize the surface morphology.

There are two kinds of imaging mode widely used in AFM measurements: contact mode and tapping modeTM. Contact mode imaging is a standard topographical imaging technique where a silicon nitride tip mounted on a cantilever is scanned across the surface. The vertical displacements of the tip lead to deflections of the cantilever, which are monitored by a laser beam deflector system with a segmented photodiode detector focused at the end of the cantilever. This is a fast and convenient way of imaging relatively hard samples. In tapping mode imaging, the cantilever and tip oscillate vertically near the cantilever's resonance frequency. Since the equilibrium separation distance between the tip and the sample is smaller than the oscillation amplitude (~ 50-100 nm), the tip strikes the sample surface periodically, thus significantly reducing the contact time.

Tapping mode is less likely to damage the sample than contact mode because it

eliminates lateral forces (friction and drag) between the tip and the sample. All the AFM measurements shown in this thesis were carried out in ambient air using tapping mode.

Calculations applied to AFM data are root-mean-square (RMS) roughness R_q , ripple wavelength and amplitude. R_q is the standard deviation of the height and it describes the spread of the height distribution about the mean value as shown in Equation 3-2 (Kiely and Bonnell, 1997). For a three-dimensional $N \times N$ image, a discrete approximation of R_q is

$$R_q = \sqrt{\frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N (h_{ij} - \bar{h})^2} \quad (3-2)$$

where $\bar{h}$ is the mean height, pixel height is h_{ij} ($1 \leq i \leq N$, $1 \leq j \leq N$).

An engineering method was used to measure ripple wavelength and amplitude. One example is shown in Figure 3.10 to demonstrate how the ripple wavelength and amplitude are measured. AFM image shows ripple formation (Figure 3.10(a)). Line profile is drawn along direction perpendicular to ripple orientation (Figure 3.10(b)). Assuming the horizontal distance between arrow A and arrow B is equal to ab , and the vertical distance between arrow C and arrow D is equal to cd , following equations can be obtained:

$$\text{wavelength} = \frac{ab}{n} \quad (3-3)$$

$$\text{amplitude} = \frac{cd}{2} \quad (3-4)$$

where n is the number of period, n is equal to 11 in this case.

After multiple measurements, average values are used as ripple wavelength and amplitude.

Figure 3.10 (a) AFM image showing ripples. (b) Line profile showing ripple wavelength and amplitude.

3.4.5 Transmission electron microscope

The JEOL JEM-2012 transmission electron microscope (TEM) operating at 200 kV was employed to study the microscopic structure of ion-induced ripple. The TEM specimen shown in Chapter 4 was prepared by the Gatan 691 precision ion polishing system (PIPS).

Chapter 4 Self-Organized Ripple Formation on Sn Surface during Ion Sputtering

4.1 Introduction

Ripples have been observed on Cu, Ag, Pt and Au surfaces irradiated with broad ion beam with very low ion energy of a few keV, as reviewed in Chapter 2. The ripple formation has been attributed to surface anisotropy and the existence of Ehrlich-Schwoebel barrier. The chapter reports ripple formation on a different metal, Sn, under the irradiation of 30 keV focused Ga^+ ions at room temperature. The experiment was carried out using various FIB incidence angles (0° , 15° , 30° , 45° and 60°) over a wide range of doses (10^{16} - 10^{18} ions/cm²). The sputtered areas were observed *in situ* using secondary electron images and the surface morphology was later carefully characterized under the optical microscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Transmission electron microscopy (TEM) was also used to characterize the ripple morphology on Sn surface irradiated with broad Ar^+ ion beam. It is found that the ripples are formed by self-organization due to anisotropic surface diffusion.

4.2 Incidence angle effect

4.2.1 Ripple formation at normal FIB incidence angle

The FIB irradiation of metallographically polished tin surface at normal incidence angle was found to produce periodic ripples. The FIB images were taken *in situ* every 2 min of sputtering time in order to show the ripple formation and evolution with increasing ion dose. Representative FIB images are shown in Figure 4.1.

After the initial 2 min of sputtering, lots of dots were formed on the surface, as shown in Figure 4.1(a). This seems to support the BH model which predicts formation of dots at normal ion beam incidence. However, careful observation of the image reveals that the dots are actually aligned in one direction. Ripples oriented in the direction of alignment were observed to form after an additional 4 min of ion sputtering, as shown in Figure 4.1(b). When the sputtering time increased further to a total of 10, 14, 16, and 20 min, ripples can be seen more and more clearly, as shown in Figures 4.1(c)-(f). The ripples could be seen even more clearly when the sputtered area was observed under the optical microscope, as shown in Figure 4.2(a). The clearer image is due to the sharp optical contrast between the valley and crest in the ripples.

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Figure 4.1 Evolution of surface morphology showing ripple formation at normal incidence angle on Sn surface with increasing sputtering time (FIB current = 1 nA, ion dose for 1 min = 7.49×10^{16} ions/cm²). All the images were taken by FIB imaging *in situ*. The arrow indicates fast scan direction for all the images.

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Figure 4.2 Surface morphology showing ripples formed at normal incidence angle in different grains. (a) Optical micrograph of ripples formed in one grain. (b) AFM image of ripples formed in another grain. The arrow indicates fast scan direction.

The observation of ripples is in contrast with the usual expectation that ion beam sputtering of surfaces at normal angle produces either self-organized dots or wells (Bobek *et al.*, 2001; Facsko *et al.*, 1999). The fact that both Figures 4.1 and 4.2(a) show the ripples aligned in the fast scan direction might suggest that the ripples were machined directly by the focused ion beam. However, this is found not to be the case for the following two reasons:

Chapter 4 Ripple Formation on Sn during Ion Sputtering

First, when sputtering time increased from 6 min to 20 min, the wavelength of the ripples was found to increase substantially (Figure 4.1). The evolution of ripple wavelength indicates a self-organized process. In addition, the ripple wavelength (in the order of magnitude of 1000 nm) is far greater than the distance between two adjacent FIB spots (around 20 nm for FIB current of 1 nA used). Therefore, the ripples could not be “written” directly. They could only be formed by self-organization.

Second, further experiments indicate that the ripples are always aligned in certain direction within any single tin crystal. That is to say, the alignment of ripples in the fast scan direction as shown in Figure 4.1 is incidental. When the fast scan direction was changed by rotation of scan direction, the ripple orientation was found to be the same, so it was no longer in the fast scan direction. Figure 4.2(b) serves as a good example to show that the ripples do not have to follow the fast scan direction.

Spontaneous formation of ripples on ion sputtered surfaces is usually caused by a competition between ion erosion and surface diffusion. Ion erosion does not select any preferential direction at normal incidence angle, compared with that at off-normal ion sputtering. Surface diffusion plays a more important role in pattern formation at normal incidence angle. The observed formation of ripples at normal incidence angle indicates the existence of anisotropic surface diffusion. Crystal structure of Sn is body centred tetragonal (Figure 4.3). Diffusion occurs preferentially along the energetically favoured crystal orientation. The anisotropic diffusion leads to the formation of ripple-like

structure.

Figure 4.3 A schematic diagram of crystal structure of Sn ($c > a$).

4.2.2 Ripple formation at off-normal FIB incidence angles

Ripples were also observed on the Sn surface at various off-normal incidence angles. Typical ripples obtained at 15°, 30° and 45° incidence angles are shown in Figure 4.4. In contrast to the prediction by the BH model (1988), the ripple orientation is not perpendicular to the projected ion beam direction. The ripple orientation is always the same within any single grain (Figures 4.4(a) and (b)), but changes from one grain to another in the same experimental condition (Figure 4.4(c)). The observations lend further support to the argument that formation of the ripples is due to crystallographically-dependent anisotropic diffusion during the ion sputtering process.

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Figure 4.4 AFM images of the ripples formed at various incident angles and similar ion dose levels. (a) 15° and 1.16×10^{18} ions/cm². (b) 30° and 1.04×10^{18} ions/cm². (c) 45° and 8.47×10^{17} ions/cm². Note that the ripples are neither perpendicular nor parallel to the projected beam direction. The irradiated areas in (a) and (b) are within the same grain, but the irradiated area in (c) is located in a different grain. The curved arrow indicates the fast scan direction, while the straight arrow indicates the projected ion beam direction.

4.3 Effect of crystallographic orientation on ripple formation

Backscattered electron imaging and optical imaging can reveal grain boundaries of the polycrystalline Sn samples, making it possible to study effect of crystallographic orientation on ripple formation. As shown in Figure 4.5, ripples of the same orientation formed in one of the grains but not in the adjacent grain, indicating clearly that the ripple formation is affected by the crystallographic orientation.

In order to verify further that the crystallographic orientation rather than ion beam direction determines the ripple orientation, irradiated areas are rotated by 30° and 90° from the original position and rastered with focused ion beam under same conditions respectively. The three pockets shown in Figures 4.6(a), (b) and (c) are located in the same grain (*i.e.*, within the same crystal), and again the ripples formed in the different pockets are aligned in the same direction even though the projected ion beam direction and fast scan direction are different. This provides further evidence to support the argument that crystallographic orientation determines the ripple formation.

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Figure 4.5 (a) Backscattered electron image showing a grain boundary and pockets irradiated at 30° incidence angle. (b) Optical image showing the same grain boundary and pockets in the same area as in (a). (c) Close-up of the pocket across the grain boundary identified in (a) and (b). Ripples can be seen in the pockets located in the left grain but not in the right grain. The curved arrow indicates the fast scan direction, while the straight arrow indicates the projected ion beam direction.

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Figure 4.6 Optical images of pockets irradiated at 45° ion incidence angle with different ion beam scan directions and different beam projection directions. (a) Original position. (b) Rotation of fast scan direction by 30°. (c) Rotation of fast scan direction by 90°. The curved arrow indicates the fast scan direction, while the straight arrow indicates the projected ion beam direction.

TEM foil of the pure Sn was prepared by 5 keV Ar^+ ion beam thinning procedure at incidence angle of 85°. The foil was observed under TEM. One of the results is shown in Figure 4.7. There were regular ripples formed at the edge of central hole milled by Ar^+ beam. The TEM sample was rotated during the Ar^+ ion thinning process in order to avoid ripple formation induced by the effect of incidence angle (Bradley and Cirlin, 1996; Carter, 1997; Mongeot *et al.*, 2000); therefore, the ripples formed on the Sn surface served well to support the argument of ripple formation due to anisotropic

surface diffusion.

The wavelength of ripple in Figure 4.7 was about 22 nm, which was much less than that induced by focused ion beam. This result might indicate that ripple wavelength is dependent on ion beam energy to some extent (Chini *et al.*, 2002).

Figure 4.7 TEM image of Sn surface bombarded with a 5 keV Ar^+ broad beam at incidence angle of 85° . The sample was rotated during the ion thinning process.

4.4 Effect of dwell time on ripple formation and sputtering yield

4.4.1 Effect of dwell time on ripple formation

Unless mentioned, dwell time used in the irradiation is fixed to be 3 μs . Results mentioned above and our published results (Qian *et al.*, 2005) show ripple formation at various incidence angles for dwell time at 3 μs . Dwell time is an important parameter

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involved in focused ion beam irradiation. However, its effect on pattern formation has been rarely studied.

Musil *et al.* (1996) reported on FIB implantation of 210 keV Si^{++} into GaAs at room temperature. A greater concentration of displaced atoms was observed for longer dwell time and shorter repetition time. Bischoff *et al.* (2001) investigated the influence of the dose rate on the damage creation in Si. 70 keV Co^{2+} and Ge^{2+} were implanted into the Si target. It was found that Si crystal, when irradiated for a fixed dose, became amorphous for long dwell-time (250 μs) but remained crystalline for short dwell-time (1 μs) (Bischoff *et al.*, 2001). Although Musil *et al.* (1996) and Bischoff *et al.* (2001) reported effect of dwell time on material damage and crystal structure during FIB implantation in semiconductors, they did not study effect of dwell time on surface morphology.

Dwell time ranging from 0.1 μs to 100 μs was used to study its effect on pattern formation. The total ion dose was fixed at 5.19×10^{17} ions/ cm^2 for varying dwell time at a fixed incidence angle of 30° . The detailed milling parameters are shown in Table 4.1. After irradiation at various dwell times, four distinct regimes for pattern formation are identified:

- formation of fine ripple in short dwell-time regime (0.1 to 2 μs);
- formation of a mixture of fine ripple and rough ripple in medium dwell-time regime (3 to 10 μs);
- formation of rough ripple in long dwell-time regime (15 to 20 μs); and

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- disappearance of ripples at longer dwell time (30 to 100 μs).

Table 4.1 Parameters used to mill the $25 \times 20 \mu\text{m}^2$ areas at 30° incidence angle and 1 nA in one single grain of Sn.

Dwell time (μs)	Number of passes	Sputtering time (min:s)
0.1	5986	8:00
1	599	8:00
2	299	7:59
3	200	8:01
10	60	8:01
15	40	8:01
20	30	8:01
30	20	8:01
100	6	8:01

Within the short dwell-time regime from 0.1 to 2 μs , ripples were formed with direction close to the fast scan direction of focused ion beam (Figure 4.8). Figures 4.8(a) and (b) shows ripple formed with wavelength of about 540 nm after irradiation with shortest dwell time of 0.1 μs . Ripples with same wavelength were also observed for dwell time of 2 μs (Figures 4.8(c) and (d)) and 1 μs (Figure 4.9).

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Figure 4.8 Ripple formation at 30° incidence angle within short dwell-time range (0.1 to 2 μs). (a) SEM image with dwell time of 0.1 μs; (b) Close-up image of (a); (c) SEM image with dwell time of 2 μs; (d) AFM image showing close-up of (c). The curved arrow indicates the fast scan direction, while the straight arrow indicates the projected ion beam direction (the same meanings for the arrows below).

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Figure 4.9 Images of pockets irradiated at fixed dwell time of 1 μs and 30° ion incidence angle with two different ion beam fast scan directions. (a) Overall SEM image from area at original position. (b) AFM close-up image of (a). (c) AFM image showing ripples after rotation of fast scan direction of 60° from the original position.

Ripple formed within short dwell-time range of 0.1 to 2 μs is called *fine ripple* to differentiate from ripple with larger wavelength and different orientation introduced at longer dwell-time. The fine ripple direction shown in Figure 4.8 is quite close to the fast scan direction of focused ion beam. It should be noted that results presented in Section 4.3 show that crystallographic orientation rather than the ion beam direction determines the ripple orientation for dwell time of 3 μs .

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In order to verify which factor determines the ripple orientation for the short dwell time, fast scan direction was rotated by 60° from the original position and raster scanned by ion beam with the same dwell time of $1\ \mu\text{s}$. Figures 4.9(a) and (b) show images obtained from the irradiated area at the original position, while Figure 4.9(c) shows the AFM image from the area irradiated after the 60° rotation. It is clear that ripple direction does not change with the rotation. The results confirm that the fine ripple direction is also determined by crystallographic orientation.

When dwell time was increased to the medium range (between 3 and $10\ \mu\text{s}$), the surface morphology changed from fine ripple to a mixture of fine ripple and much broader and rougher ripple, as shown in Figure 4.10.

For the longer dwell-time regime from 15 to $20\ \mu\text{s}$, only rough ripple was observed, as shown in Figure 4.11. For the rough ripple observed for dwell time range of 3 to $20\ \mu\text{s}$, the wavelength is about $1.7\ \mu\text{m}$, which is much larger than wavelength of fine ripples produced with short dwell time of 0.1 to $2\ \mu\text{s}$ for the same ion dose used (see Table 4.1). The orientation of the rough ripples also differs from that of the fine ripples.

When dwell time was further increased to $30\ \mu\text{s}$ and above, ripple could not be observed. Figure 4.12 shows surface irradiated at a dwell time of $100\ \mu\text{s}$.

Figure 4.13 shows the root-mean-square roughness measured from AFM images as a function of dwell time. The same AFM scan size ($15 \times 15\ \mu\text{m}^2$) was used for all the

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measurements. The figure shows increase in RMS roughness with increasing dwell time from 0.1 to 20 μs and the trend of surface smoothing when dwell time is further increased.

Figure 4.10 Ripple formation at 30° incidence angle within medium dwell-time range (3 to 10 μs). (a) SEM image showing ripple formed at dwell time of 3 μs . (b) AFM Close-up image of (a). (c) SEM image showing ripple formed at dwell time of 10 μs . (d) Close-up of (c).

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Figure 4.11 Ripple formation at 30° incidence angle within longer dwell-time range (15 to 20 μs). (a) SEM image showing ripple formed at dwell time of 15 μs . (b) Close-up of (a). (c) SEM image showing ripple formed at dwell time of 20 μs . (d) AFM image showing close-up of (c).

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Figure 4.12 Images showing surface morphology after irradiation at 30° incidence angle and with dwell time of $100 \mu\text{s}$. (a) SEM image showing the overall picture. (b) AFM image showing the close-up of (a).

Figure 4.13 RMS roughness as a function of dwell time.

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The phenomenon that ripple changes its orientation with increasing dwell time on Sn surface is quite similar with ripple rotation on Ag (110) (Valbusa *et al.*, 2003) and Cu (110) (Rusponi *et al.*, 1998a) surfaces by increasing the substrate temperature. The resemblance makes us to examine whether effect of dwell time on Sn surface might be due to the change of temperature at various dwell times.

Melngailis (1987) used a simple way to estimate the temperature rise due to focused ion beam. As shown in Figure 4.14, ion beam with radius r is incident on a semi-infinite solid. A spherical coordinate system is centered at the point of impact with radial coordinate ρ .

Figure 4.14 Schematic diagram showing heat flow at point of ion beam incidence. Ion beam has radius r . In spherical coordinates ρ is the radius from the center of the beam on the surface.

For a beam of voltage V , current A and current density J , the total input power is VA or $VJ\pi r^2$. Assuming that radiative (or other) heat loss from the surface is negligible

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and that the input power is equal to the thermal energy current flowing out of a hemisphere of radius ρ into the semi-infinite solid,

$$VJ\pi r^2 = -K2\pi\rho^2 \frac{dT}{d\rho} \quad (4-1)$$

where K is the thermal conductivity and T is the temperature. When Equation 4-1 is integrated, the temperature rise above the background at a radius ρ can be obtained,

$$T(\rho) - T(\infty) = \frac{VJr^2}{2K\rho} \quad (4-2)$$

Consider $\rho = r$, *i.e.*, the point where Equation 4-2 predicts the highest temperature. The maximum temperature rise occurs to the point where ρ is equal to the ion beam radius. In our case, $V = 30$ kV, $r = 25$ nm for FIB current of 1 nA used, and $J = 51$ A/cm² (see Table 3.1) and taking the thermal conductivity of Sn (K) = 62.7 W·m⁻¹·K⁻¹ (Bauccio, 1993), the temperature rise is calculated to be 3 K and thus negligible. Therefore, the experimental results cannot be explained by this calculation.

The diffusive term in the nonlinear theory reviewed in Chapter 2 describes only an isotropic diffusion. It does not take into account that the adatom (vacancy) mobility in a single crystal is actually biased by different diffusion rates along the two crystallographic directions. Since crystal structure of Sn is body centred tetragonal, the surface diffusion is anisotropic. The experimental results presented in this section and the two previous ones all lead to the conclusion that the formation of ripples on Sn surface is due to anisotropic surface diffusion. The study on the effect of dwell time

helps to gain additional knowledge that the preferential diffusion direction is affected by dwell time.

4.4.2 Effect of dwell time on sputtering yield

In project, dwell time was varied with the primary objective of studying how dwell time affects formation of the surface patterns. The experimental work carried out also presents a good opportunity to study effect of dwell time on the sputtering yield. Areas within the same Sn grain irradiated with different dwell times were characterized using AFM to find the sputtering depth. The depth and fixed frame area ($25 \times 20 \mu\text{m}^2$) were used to calculate the volume and mass of material removed. The number of ions used to remove the material can be calculated easily from the dose recorded; therefore, sputtering yield can be calculated as the number of removed Sn atoms per incident ion. The results are shown in Figure 4.15. It is interesting to note from the figure that the sputtering yield increases with dwell time.

Sputtering yield during FIB micromachining was measured for many types of materials, including Si (Pellerin *et al.*, 1990; Steckl and Chyr, 1999; Yamaguchi *et al.*, 1985), GaN (Steckl and Chyr, 1999), SiC (Steckl and Chyr, 1999), Al_2O_3 (Steckl and Chyr, 1999), GaAs (Pellerin *et al.*, 1990; Young *et al.*, 1993), and InP (Pellerin *et al.*, 1990; Young *et al.*, 1993). However, effect of dwell time on sputtering yield is not studied in any of the references cited with the only exception of the work by Yamaguchi *et al.* (1985) and Pellerin *et al.* (1990).

Figure 4.15 Sputtering yield as a function of dwell time on Sn surface (30° incidence angle and 5.19×10^{17} ions/cm²).

Yamaguchi *et al.* (1985) reported the effect of scanning rate (dwell time integrated over the scan area) on sputtering yield of Si (100) and material redeposition. Two $10 \times 10 \mu\text{m}^2$ areas were milled with 30 kV Ga^+ ion beam at 0.5 nA for the same ion dose. A flat bottom trench was produced for fast scan repeated 200 times, while a highly asymmetric trench was milled for one time slow scan. The sputtering depth of slow scan was found to be much deeper than that of fast scan. Yamaguchi *et al.* (1985) did not mention “dwell time” in their study, but their results indicate that longer dwell time (*i.e.*, slow scan) leads to larger sputtering yield for the material they studied. They attributed the larger sputtering yield to the effect of incidence angle and the nonlinear effect caused by the overlapping of cascades and asymmetric shape to the redeposition.

Pellerin *et al.* (1990) observed enhanced removal rates at long dwell times during FIB micromachining of Si, GaAs and InP. The authors tentatively attributed the increase of sputter rate to the effect of incidence angles. The larger oblique incidence angles formed at longer dwell times might be a factor for the increase in sputtering yield; however, this factor can hardly explain such a large difference in sputtering yield (by 3 times when dwell time changes from 0.1 to 100 μ s, as shown in Figure 4.15).

A simple model is proposed here to explain the variation of sputtering yield with dwell time. Figure 4.16 schematically shows two scenarios of ion sputtering, the classical sputtering process (Figure 4.16(a)) and faster sputtering due to the edge effect (Figure 4.16(b)). Comparison of the two scenarios shows clearly that sputtering yield can be much increased when the focused ion beam irradiates at the edge (as shown in Figure 4.16(b)) because of ejection of atoms from the sidewall.

When dwell time is small, each pixel is irradiated with a small number of ions, so the step between the pixel being irradiated and the one which has just been irradiated is very small, leading to small edge effect. In contrast, when dwell time is large, each pixel is irradiated with a large number of ions, so the step between the pixel being irradiated and the one which has just been irradiated is very large, and this results in large edge effect and thus much higher sputtering yield.

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(a) Classical sputtering

(b) Edge effect

Figure 4.16 Illustrations showing effect of edge on sputtering yield. (a) Classical sputtering with ejection of atoms from top surface only; (b) Edge-enhanced sputtering due to ejection of atoms from sidewall as well as from the top surface.

The sputtering yield was also calculated with SRIM-2003.26 (a Monte Carlo simulation code) available online from the Internet. 1000 incident Ga^+ ions were used for simulation. The input parameters for the simulations are summarized in Table 4.2. Figure 4.17 shows the damage cascade and ion trajectories simulated at 30° incidence angle. Implantation depth of Ga ions is calculated to be 16 ± 9 nm. The sputtering yield from simulation is 9.17 atoms/ion. It is very interesting to note that the simulated result is very close to the measured sputtering yield for the shortest dwell time of $0.1 \mu\text{s}$ (Figure 4.15). The numerical simulation did not consider “edge effect”, so the simulated result is valid only when the “edge effect” is minimal at the short dwell time.

Table 4.2 Parameters used in SRIM MC simulation of Sn (Ziegler, 2003)

Voltage (keV)	Incidence angle (°)	Surface binding energy (eV)	Lattice binding energy (eV)	Displacement energy (eV)	Density (g/cm ³)
30	30	3.12	3	25	7.282

Figure 4.17 SRIM MC simulations for 30 keV Ga^+ into Sn at 30° incidence. (a) Damage cascade; (b) Ion trajectories in Sn. The arrows indicate the incident directions of Ga^+ .

4.5 Effect of ion dose on ripple formation

The observed surface morphology was further studied quantitatively. Figure 4.18 shows ripple amplitude as a function of ion dose. It can be seen that the amplitude increases linearly with increasing ion dose for the whole range of ion doses studied (2×10^{17} – 8.5×10^{17} ions/cm²). It should be noted, however, that ripple amplitude saturation has been observed by others for very high ion dose (around 10^{19} ions/cm²), *e.g.*, by Erlebacher *et al.* (1999) on Si surface. They found that ripple amplitude will saturate after initial short period of exponential increase. Therefore, the increase of the ripple amplitude in Figure 4.18 may be just in the first stage.

The relationship between ripple wavelength and ion dose at 30° and 45° incidence angles is shown in Figure 4.19. It can be observed that the wavelength is not sensitive to the change of ion dose in the dose range studied. It should be noticed that crystal orientation also has influence on ripple wavelength. Ripple wavelength at 30° incidence in one grain is different from that at 45° incidence in another grain.

In many previous studies, ripple wavelength is found to be independent of ion dose (Makeev *et al.*, 2002). However, it is also reported that wavelength increases with ion dose following a scaling law $\lambda \propto t^z$ (t is sputtering time or ion dose, and z is material-dependent numerical constant) on metals (Habenicht *et al.*, 2002; Rusponi *et al.*, 1998b). The experimental results in the present study are in agreement with the

dose-independent wavelength. However, it should be born in mind that the observation is valid for the dose range above 10^{17} ions/cm². In the very early stage of ripple formation, the scaling law might be applicable.

Figure 4.18 Ripple amplitudes measured in the same grain as a function of ion dose at 45° incidence angle. (Dwell time used for sputtering is 3 μ s)

Figure 4.19 Ripple wavelengths measured in the same grain for 30° incidence angle and in another grain for 45° incidence angle and shown as a function of ion dose. (Dwell time used for sputtering is 3 μ s)

The time evolution of ripple formation at 30° incidence angle was investigated *in situ*, as shown in Figure 4.20. SEM images were taken *in situ* every 1 min of ion irradiation. Ion dose for 1 min is 6.49×10^{16} ions/cm². Irradiation was carried out at 30° incidence angle and with dwell time of 15 μ s. As shown in Figure 4.20(b), ripples were formed immediately after 1 min of irradiation. With sputtering time increasing to 10 min, the ripple amplitude and wavelength increase. When the accumulated sputtering time is increased from 10 to 15 min, the ripple wavelength saturation is observed. The ripple orientation for the sputtering time studied is not perpendicular to the projected ion beam direction. This again provides complementary support to what discussed in Sections 4.3 and 4.4.

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Figure 4.20 SEM images showing ripple formation at 30° incidence angle with increasing sputtering time (ion dose for 1 min = 6.49×10^{16} ions/cm²). Dwell time used for sputtering is 15 μ s.

4.6 Summary

Ripple was formed on Sn surface both at normal and off-normal incidence angles. The experimental results show that crystallographic orientation determines ripple direction. The ripple wavelength is independent of ion dose for short dwell time (3 μ s), but increases with ion dose first and stabilizes under larger ion dose for long dwell time (15 μ s). Ripple amplitude is observed to increase with ion dose used.

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Two kinds of characteristic ripples were observed over a large range of dwell time varying from 0.1 μs to 100 μs at 30° incidence angle. One kind of ripples with wavelength of 540 nm was found for short dwell-times (0.1 to 2 μs) and the other kind of ripples with wavelength of 1.7 μm was observed for long dwell-times (3 to 20 μs). Orientation is different for the two kinds of ripples.

The sputtering yield increases with dwell time significantly. Empirical observations are compared with SRIM MC simulations. It is found that the sputtering yield calculated from simulation tallies with the sputtering yield observed for the shortest dwell time. A model is proposed to explain the larger sputtering yield under longer dwell time. As a result of sidewall created by long dwell time, the escape probability of surface atoms increases dramatically and therefore sputtering yield increases. Anisotropic surface diffusion was taken into account to explain ripple formation on Sn surface.

Chapter 5 Self-Organization of Ripples on Ti Sputtered with Focused Ion Beam

5.1 Introduction

Surface morphology on low-melting-point metal Sn ($T_m=232\text{ }^\circ\text{C}$) has been investigated after irradiation with focused ion beam, as presented in Chapter 4. Ti with high melting point ($1670\text{ }^\circ\text{C}$) was used in this chapter to complement the study on metals irradiated with focused ion beam.

30 keV focused Ga^+ ions were used to raster the metallographically polished surface of commercially pure Ti (CP Ti) at various FIB incidence angles over a wide range of doses (10^{16} - 10^{18} ions/ cm^2) at room temperature. The sputtered surfaces were observed *in situ* using FIB imaging and later carefully characterized *ex situ* under scanning electron microscope (SEM) and atomic force microscope (AFM). Ripples were observed on the irradiated surfaces even at the normal FIB incidence angle. The ripple evolution is analysed as functions of surface diffusion, surface crystallographic orientation, ion dose and incidence angle. It is found that the ripples are formed due to anisotropic diffusion at normal incident angle or at a small angle of 15° but the ripple formation at larger incident angles is affected by curvature-dependent ion erosion as well as by the anisotropic surface diffusion.

5.2 Effect of anisotropic surface diffusion on ripple formation

FIB irradiation of Ti surface at normal incidence angle was found to produce ripples. Ripples were formed spontaneously when ion dose was higher than 10^{18} ions/cm² with normal incidence irradiation. Figure 5.1 shows ripples formed at ion dose of 2.40×10^{18} ions/cm². Figure 5.1(a) is an overall SEM image of the irradiated area. A magnified view is shown in Figure 5.1(b). Ripples formed in grain 1 as indicated in Figure 5.1(a) were further characterized using AFM and are shown in Figure 5.1(c). The line profile along the direction perpendicular to the ripple orientation is shown in Figure 5.1(d). Grain boundaries can be seen clearly in Figures 5.1(a) and (b). The orientations of the ripples formed in different grains are different. However, the ripple orientation is always the same within any single grain.

Figure 5.2 shows ripple formation on Ti surface irradiated at normal incidence angle but with higher ion dose (4.79×10^{18} ions/cm²). The overall picture of irradiated area is shown in Figure 5.2(a). Three of the grains shown in the figure are labelled as 1, 2 and 3 respectively. Ripples in grains 1, 2 and 3 are shown at higher magnifications in Figures 5.2(b), (c) and (d) respectively. It is clear that grains irradiated with the same FIB parameters display ripples with different orientations. It may be argued that the ripple orientation in each grain corresponds to energy favoured crystallographic orientation.

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Figure 5.1 Images showing ripple formation on Ti surfaces irradiated with ion dose of 2.40×10^{18} ions/cm² at normal incidence angle. (a) SEM image of irradiated surface. (b) Close-up. (c) AFM image of grain 1 labeled in (a); (d) AFM line profile along the direction perpendicular to direction of ripples shown in (c).

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Figure 5.2 SEM images showing ripple formation on Ti surface irradiated with ion dose of 4.79×10^{18} ions/cm² at normal incidence angle. (a) Overall image; (b) Close-up of ripples in grain 1 indicated in (a); (c) Close-up of ripples in grain 2 indicated in (a); (d) Close-up of ripples in grain 3 indicated in (a).

It is well known that dots and wells will form after irradiation at normal angle (Bobek *et al.*, 2001; Facsko *et al.*, 1999). In contrast to this expectation, ripples were observed to form at normal incidence angle in the experiments. Ti at room temperature has the HCP (hexagonal close-packed) structure with six atoms in the unit cell with $c = 4.6833 \text{ \AA}$ and $a = 2.9504 \text{ \AA}$, leading to a density ρ of 4.507 g/cm^3 . The melting point of Ti is $1670 \text{ }^\circ\text{C}$ (Bauccio, 1993). The surface thermal diffusion dependent on temperature is not effective

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since room temperature is very low compared with the melting point T_m (about 15% T_m in terms of K). However, ion bombardment is known to enhance the surface diffusion (Makeev and Barabási, 1997). Anisotropic surface diffusion induces the ripple formation even at normal incidence angle at relatively “low” temperature (Costantini *et al.*, 2001; Rusponi *et al.*, 1998a).

5.3 Effect of crystallographic orientation on ripple formation

According to the well-accepted Bradley-Harper model (1988), the direction of ripples should be either parallel or perpendicular to the projected ion beam direction at off-normal incidence angle. However, ripples were obtained on Ti surfaces at off-normal incidence, whose direction was found to be independent of ion beam direction. The results are similar to those for Sn presented in Chapter 4.

A typical example showing effect of crystallographic orientation on ripple formation is given in Figure 5.3. The surface morphology was characterized using SEM and AFM. Dots and ripples were formed in different grains of the irradiated area under the same ion sputtering condition. As seen from Figures 5.3(c) and (d), the dots were decorated on the ridge-like ripples. The diameter of dots varies from 200 nm to 400 nm. Ripples formed in one single grain have the same orientation, but the directions are varied in different grains, as shown in Figures 5.3(b), (e) and (f).

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Figure 5.3 Images showing pattern formation on Ti surface irradiated at 15° incidence angle with ion dose of 4.63×10^{18} ions/cm². (a) Overall SEM image; (b) Close-up; (c) SEM magnified view of pattern in grain1 labeled in (a); (d) AFM image of pattern in grain 1 labeled in (a); (e) AFM image of pattern in grain 2 labeled in (a); (f) AFM image of pattern in grain 3 labeled in (a). The curved arrow indicates fast scan direction for all images, and the straight arrow indicates projected ion beam direction for all images.

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Ion dose delivered to the irradiated surface is also important to reveal the effect of ion erosion on morphological change in different grains. Figure 5.4 shows ripple formation under increasing ion dose. As shown in Figure 5.4(a), grain effect on ripple formation cannot be revealed for ion dose of 5.79×10^{17} ions/cm². Above this ion dose level, effect of crystallographic orientation on ripple formation can be seen clearly, as shown in Figures 5.4(b)-(d).

The images shown in Figures 5.3 and 5.4 imply that crystallographic orientation plays an important role in surface morphology evolution. After irradiation, dots were formed in the grain with certain crystallographic orientation, whereas ripple-like structures were formed in the grains with other orientations. The ripple direction is determined by crystallographic orientation rather than ion beam direction, again supporting the ripple formation mechanism proposed in Chapter 4.

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Figure 5.4 SEM images showing ripple formation with increasing ion dose at 15° incidence angle. (a) Ion dose is 5.79×10^{17} ions/cm²; (b) Ion dose is 1.16×10^{18} ions/cm²; (c) Ion dose is 2.32×10^{18} ions/cm²; (d) Close-up of (c).

5.4 Effect of ion beam incidence angle on ripple formation

When the Ti surface was irradiated at normal incidence angle (see Section 5.2) or at a small incidence angle of 15° (see Section 5.3), the ripple orientation was determined by the crystallographic orientation rather than the ion beam direction. However, when the incidence angle was increased further to 30° , 45° and 60° , the ripple orientation was increasingly influenced by the ion beam projection direction, as shown in Figures 5.5-5.7.

With incidence angle increasing, the role of incidence angle on ripple formation is more and more important. Figure 5.5 shows surface patterns formed at 30° incidence angle at ion dose of 2.08×10^{18} ions/cm² (Figures 5.5(a) and (b)) and at higher ion dose of 4.15×10^{18} ions/cm² (Figures 5.5(c) and (d)). It should be noted that the ripples in different grains orientate nearly perpendicular to the ion beam direction as predicted by the classical BH model (Bradley and Harper, 1988). This fact reveals that ion beam direction plays greater role in the ripple direction rather than crystallographic orientation at this incidence angle. However, it should be noted that crystallographic orientation still plays a role in ripple formation. For example, Figure 5.5 shows that the wavelength of ripples is different in various grains, though the ripple orientation is always perpendicular to the ion beam.

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Figure 5.5 SEM images showing the ripple formation at 30° incidence angle. (a) Overall picture of area irradiated with ion dose of 2.08×10^{18} ions/cm²; (b) Close-up of (a); (c) Overall picture of area irradiated with ion dose of 4.15×10^{18} ions/cm²; (d) Close-up of (c).

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When the incidence angle was increased to 45° , curved ripples were formed, as shown in Figure 5.6. Figures 5.6(a) and (b) are viewed by FIB imaging at an angle of 45° (*i.e.*, viewed along the ion beam projection direction). If the same area is viewed at normal angle using SEM, the irradiated surface displays as fragmented structure, as shown in Figures 5.6(c) and (d).

FIB and SEM imaging were used to compare the morphology on areas irradiated with 60° incidence angle at different tilt angles, as shown in Figure 5.7. Curved ripples formed at 45° developed to networks at 60° incidence angle, as shown in Figures 5.7(a) and (b). Those networks were in fact rod-shaped features viewed at normal angle using SEM, as shown in Figures 5.7(c) and (d).

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Figure 5.6 Images showing curved ripples after irradiation at 45° incidence angle and with ion dose of 1.69×10^{18} ions/cm². (a) and (b) Curved ripples imaged by FIB at a tilt angle of 45° from surface normal; (c) and (d) Curved ripples imaged by SEM at normal angle.

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Figure 5.7 FIB and SEM images showing curved ripples after irradiation at 60° incidence angle and with ion dose of 2.40×10^{18} ions/cm². (a) and (b) Curved ripples imaged by FIB at a tilt angle of 60° from surface normal; (c) and (d) Curved ripples imaged by SEM at normal angle.

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Such curved ripples have never been reported and no existing models can be used to explain their formation. It is proposed that there are two factors acting on the pattern formation: one is crystallographic orientation-dependent anisotropic surface diffusion; the other is incidence-angle dependent ion erosion. The interaction and competition between these two mechanisms induces pattern formation observed here. At small incidence angles (from 0° to 15°), ripple formation is mainly induced by anisotropic surface diffusion and ripple orientation is determined by crystallographic orientation. The effect of FIB incidence angle on pattern formation becomes more and more important when the angle increases. When the two forces are equally present on the irradiated surface, the surface profile looks like curved ripples when viewed from tilt angle and fragmented rods when viewed at 0° to the surface.

Experiment carried out by Rusponi *et al.* (1998a) on Cu (110) at low temperature (180 K) lends some support to the argument. Rusponi *et al.* (1998a) reported that ripple formed at 45° incidence angle was oriented along $\langle 001 \rangle$ without any relationship with projected ion beam direction. However, when the incidence angle was increased to 70° , the ripples were perpendicular to ion beam direction.

5.5 Effect of crystallographic orientation on sputtering yield

In addition to dwell time presented in Chapter 4, crystallographic orientation also affects sputtering yield. As shown clearly in Figures 5.3, 5.6, 5.7 and 5.8, different grains have different sputtering depth under the same sputtering conditions. Figure 5.8 shows one

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representative area displaying the effect of grain orientation on sputtering depth (sputtering yield). Differences in sputtering depth for various grains are shown in the line profiles in Figures 5.8(b) and (c).

It has been reported that the sputtering yield varied with the crystal orientations (Onderdelinden, 1966; Southern *et al.*, 1963; Yurasova and Eltekov, 1982). The sputtering yield minima were observed on Cu single crystals in the directions where the crystal is most transparent to the ion beam and the maxima in the directions of least transparency (Onderdelinden, 1966). Southern *et al.* (1963) reported that the yield from Cu monocrystals was strongly dependent on orientation and the effect was more pronounced as the energy was increased. The mean free path for the ion is largest for those bombarding directions in which the crystal is transparent, while it is smallest for directions, where the crystal is not transparent (Rol *et al.*, 1960). The transfer of the energy and momenta is most effective in the close packed directions due to the focusing mechanism (Southern *et al.*, 1963). Therefore, most of the surface atoms acquire momenta from the atoms of the lower rows only in these close-packed directions. If the energy transferred to an atom exceeds its surface binding energy, an atom will be ejected from the crystal. The predominant sputtering of substances occurs in the close packed directions.

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Figure 5.8 The difference of height in various grains for area irradiated at 45° incidence and with ion dose of 3.39×10^{18} ions/cm². (a) AFM image; (b) Line profile from top to bottom; (d) Line profile from left to right.

5.6 Summary

The formation of self-organized periodic structures during sputtering of Ti surface was observed both at normal and off-normal incidence angles at room temperature. Ripples on surface of a single crystal were oriented in the same direction, but the ripple orientation changed with the crystallographic orientations. When the ion beam was incident at a small angle of up to 15° , the ripple direction was determined by the crystallographic orientation. However, when the FIB incident angle was increased to 30° , 45° or 60° , the ripple orientation was progressively influenced by the ion beam direction and in some cases curved ripples or fragmented rods viewed from different angles occurred at high ion doses. It was also found that the sputtering yield varied with the crystal orientations.

The morphological evolution from the well-developed straight ripples to the curved ones is never observed. The formation of ripples is attributed to the competition between the formation of ripples due to anisotropic surface diffusion and the formation of incidence-angle dependent ripples determined by BH model.

Chapter 6 Pattern Formation on ZnO Thin Film Irradiated with Focused Ion Beam

6.1 Introduction

Zinc oxide (ZnO) is a multifunctional material that has attracted much attention recently. The nanostructures of ZnO could have novel applications in optoelectronic nanodevices (Huang *et al.*, 2001), sensors, transducers, and biomedical science (Wang, 2004).

In this study, 30 keV focused Ga^+ ions were used to raster ZnO thin film at various FIB incidence angles over a wide range of doses at room temperature to investigate the evolution of surface topography. Surface diffusion biased by Ehrlich-Schwoebel barrier can be introduced to account for ripple evolution.

6.2 Pattern formation on ZnO thin film

ZnO nanowires have been synthesized by various methods, *e.g.* laser ablation (Ataev *et al.*, 1997), electrodeposition (Li *et al.*, 2000), chemical or physical vapor deposition (Chen *et al.*, 2004; Saitoh *et al.*, 1999; Chiou *et al.*, 2003; Huang *et al.*, 2001), thermal evaporation using ZnO powders (Lee *et al.*, 2003; Pan *et al.*, 2001), *etc.*

The ZnO studied in the project was ZnO (002) film of 200 nm in thickness. It was prepared by a research collaborator for certain device applications. The preparation

procedure involved thermal oxidation of a silicon substrate to produce a layer of SiO_2 of 400 nm in thickness and subsequent deposition of ZnO film by the filtered cathodic vacuum arc technique. The sample prepared is shown in Figure 6.1.

Figure 6.1 Schematic image showing ZnO thin film on SiO_2/Si substrate.

The topography of as-deposited ZnO film was measured using AFM. Bump-like structures were distributed on as-deposited surfaces, as shown in Figure 6.2. The ZnO film in the as-deposited condition was then irradiated at room temperature with 30 kV Ga^+ ion using the Micrion FIB and Quanta 3D FIB. The current was fixed at 1 nA. The sputtering time was varied to investigate the evolution of surface morphology over a wide range of doses (10^{16} - 10^{18} ions/ cm^2).

Figure 6.2 AFM images of as-deposited ZnO surface.

The surface morphologies irradiated with various ion doses at incidence angles of 0° , 15° and 30° resemble the unirradiated surfaces and show the development of mound structures. However, further increase of the incidence angle shows beginning of distinct change of the surface morphology.

Figure 6.3 shows ripple evolution with increasing ion doses at 45° incidence angle. After irradiation with ion dose of 1.06×10^{17} ions/cm² (Figure 6.3(a)), worm-like features appear on the surfaces. Increasing ion dose to 2.12×10^{17} ions/cm², the worm-like features coalesce with each other and are aligned perpendicular to the ion beam projection direction (Figure 6.3(b)). The ripples are well developed and the corrugation increases with ion dose increasing to 4.24×10^{17} ions/cm² and 8.47×10^{17} ions/cm² (Figures 6.3 (c) and (d)).

Figure 6.3 AFM images showing morphology of ZnO surfaces irradiated with 45° incidence angle at different ion doses. (a) 1.06×10^{17} ions/cm². (b) 2.12×10^{17} ions/cm². (c) 4.24×10^{17} ions/cm². (d) 8.47×10^{17} ions/cm². Horizontal arrows represent beam fast scan direction and vertical arrow represent projected ion beam direction (the same meaning for arrows below).

Similar surface evolution process occurs to the surfaces irradiated with 60° incidence angle, as shown in Figures 6.4(a)-(d). Ripple direction shown in Figures 6.3 and 6.4 does not depend on the crystallographic orientation, and it is always perpendicular to the projected ion beam direction.

Figure 6.5 gives a specific example of ripple line profile formed with ion dose of

8.47×10^{17} ions/cm² at 45° incidence angle. It is clear that the sinusoidal periodic structures perpendicular to the ion beam direction are with wavelength of about 320 nm.

Figure 6.4 AFM images showing morphology of ZnO surfaces irradiated with 60° incidence angle at different ion doses. (a) 7.49×10^{16} ions/cm². (b) 1.5×10^{17} ions/cm². (c) 3×10^{17} ions/cm². (e) 6×10^{17} ions/cm².

Figure 6.5 (a) Ripples topography observed by AFM at 45° incidence angle with a dose of 8.47×10^{17} ions/cm² and (b) the corresponding line scan showing the wavelength of ripples. The ripple orientation is perpendicular to the ion beam projection.

The relationship between ripple wavelength λ and sputtering time t is plotted in Figure 6.6. The solid lines represent the fit lines. The ripple wavelength at 45° incidence angle as well as at 60° incidence angle grows with the sputtering time following power law $\lambda \propto t^\beta$ with $\beta = 0.21$.

Figure 6.6 The ripple wavelength λ as a function of the sputtering time t on ZnO film at incidence angles of 45° and 60° respectively (ion flux for 45° incidence = 8.83×10^{14} ions/(cm²s), ion flux for 60° incidence = 6.23×10^{14} ions/(cm²s)). The solid lines represent the fit according to the power law scaling relation $\lambda \propto t^\beta$ with $\beta = 0.21$.

Figure 6.7 The RMS roughness σ as a function of the sputtering time t on ZnO film at incidence angles of 45° and 60° respectively (ion flux for 45° incidence = 8.83×10^{14} ions/(cm²s), ion flux for 60° incidence = 6.23×10^{14} ions/(cm²s)). The solid lines represent the fit according to the exponential law scaling relation $\sigma \propto e^{nt}$ with $n = 0.0026$.

Figure 6.7 shows the rms roughness σ as a function of the sputtering time t at incidence angles of 45° and 60° respectively. Surface roughness irradiated with both 45° and 60° incidence angles grows exponentially with sputtering time. The scaling law follows $\sigma \propto e^{nt}$ with $n = 0.0026$. The roughness for as-deposited ZnO surface was 18 nm. Therefore irradiated surfaces undergo smoothing effects for short sputtering time (low ion dose).

6.3 Discussion

Since the thickness of ZnO thin film is only 200 nm, it is important to know whether the ripples shown in Figures 6.3-6.5 were formed on the ZnO film. EDP (End Point Monitor) on FIB machine served this purpose. It detected the absorbed sample current during milling process.

Absorbed current generated while milling through a multi-layered structure can be used to identify different materials in the structure (Davis and Khamsehpour, 1993). During ion milling, a current flowing from specimen to the ground depends on the beam current and on the number of generated secondary electrons and ions. The number of secondary electrons and ions generated during milling is material dependent. Therefore, different materials can be identified by monitoring the current flow to the ground (absorbed current). During this process, an ammeter detects the current flow. While milling a multi-layered structure as Ga^+ ions mill through one layer to the next, the current

generated changes thus identifying different materials.

Figure 6.8 shows an EPD graph for ZnO thin film structure, the figure is a plot of measured current versus sputtering time. The FIB milling conditions were: 45° incidence angle, FIB current of 3 nA, irradiated area of $25 \times 20 \mu\text{m}^2$ and milling time of 10 min. The sudden increase and decrease in sample current, as shown in Figure 6.8, indicates the transition from ZnO milling to SiO₂ milling. This illustrates the method to monitor the milling process. In the study of the surface pattern formation, FIB parameters used were different, but the same method was used to make sure the results presented in Figures 6.3-6.7 were obtained from ZnO film.

Figure 6.8 EPD graph shows the current signal from different materials.

When ion dose increased till the ZnO film was milled away, ion erosion occurred to SiO₂ film. Ripples disappeared and only random surface features were observed on the irradiated SiO₂ surface, as shown in Figure 6.9.

Figure 6.9 AFM images showing pattern formation on the SiO₂ film at different incidence angles and similar ion doses. (a) 45°, 1.69×10^{18} ions/cm². (b) 60°, 1.2×10^{18} ions/cm².

Ripples were also observed on polycrystalline metal thin films (Au, Pt, Ag, Cu and Co) at incidence angles of 60°, 70° and 80° irradiated with 16.7 keV Ar⁺ ion beam (Karmakar and Ghose, 2004). At 60° incidence angle, weakly pronounced ripples appeared with orientation parallel to the ion beam direction, especially in Co and Cu films. At 70° and 80° incidence angles, ripples were developed with orientation perpendicular to the projected ion beam direction. However, no ripples were formed at incidence angles ranging from 0° to 50° (Karmakar and Ghose, 2004). It might be inferred that ripple is much easier to form under larger incidence angles and ripple orientation formed on thin films can be predicted by BH model.

Chapter 6 Pattern Formation on ZnO Irradiated with FIB

The observed scaling law $\lambda \propto t^\beta$ disagreed with BH model (Bradley and Harper, 1988) based on surface-curvature-dependent erosion rate, which predicts temporal independence of wavelength. For many semiconductors and amorphous materials, the observed wavelength does not change even with extended sputtering time (Chason and Aziz, 2003; Chason *et al.*, 2001). Constant wavelength of ripples has also been observed on Cu (100) surfaces at grazing angle when the substrate temperature was below 200 K (Dijken *et al.*, 2001). However similar power law relationship has been observed in some materials like Cu (110) ($\beta = 0.26 \pm 0.02$) (Rusponi *et al.*, 1998b), Ag (100) ($\beta = 0.24 \pm 0.03$) (Valbusa *et al.*, 2003), Au (111) ($\beta = 0.27 \pm 0.02$) (Murty *et al.*, 1998) and SiO₂ ($\beta = 0.15 \pm 0.01$) (Flamm *et al.*, 2001).

BH model predicts an exponential dependence of the ripple amplitude, and consequentially, an exponential dependence of the rms surface roughness. Therefore the exponential growth of surface roughness agrees with the BH model. It should be noted that amplitude saturation has been observed on Si surface by Erlebacher *et al.* (2000). They found that ripple amplitude will saturate after initial short period of exponential increase. Therefore, the increase of the ripple amplitude in Figure 6.7 may be just in the initial stage.

Barabási and Stanley (1995) have pointed out that sputtering erosion and atom deposition are two processes with a lot of common features. It is noted that the observed scaling law appear very similar to those measured on substrates during growth process with an Ehrlich-Schwoebel barrier at the step edges (Stroscio *et al.*, 1995; Thurmer *et al.*, 1995;

Zuo and Wendelken, 1997). Therefore, the ripple coarsening was attributed to the effect of Ehrlich-Schwoebel barrier on the interlayer diffusion of adatoms (Rusponi *et al.*, 1998b).

6.4 Summary

Pattern formation has been investigated on ZnO thin film surfaces at incidence angles of 0°, 15°, 30°, 45° and 60°. Ripples were formed on ZnO thin films only at 45° and 60° incidence angles. Ripple orientation was always perpendicular to the projected ion beam direction. Both ripple wavelength and surface roughness increased with sputtering time (ion fluence). The ripple formation on thin films can be explained by inclusion of Ehrlich-Schwoebel barrier in well-accepted BH model. The simplicity and generality of the results shown above are expected to be easily extended to other systems of technological interest, *e.g.* tailoring the magnetic properties of thin film by changing the surface morphology (Sekiba *et al.*, 2004).

Chapter 7 Self-Organization on Si (100) Surface Irradiated with Focused Ion Beam

7.1 Introduction

Si is a technologically important material. Sputter induced surface rippling on Si was observed by various researchers for different incidence angles, but broad ion beam was used in most cases (Erlebacher *et al.*, 1999; Karmakar and Ghose, 2004; Vajo *et al.*, 1996). In this study, Si (100) surface was irradiated with 30 keV focused ion beam. Effects of incidence angle, dwell time, ion dose and beam overlap were investigated. Surface morphology of irradiated area was characterized using scanning electron microscope (SEM) and atomic force microscope (AFM).

7.2 Surface morphology irradiated at normal incidence angle

There always exists native oxide on Si surface. The thickness of native oxide is usually 1-2 nm in thickness (Goswami and Dev, 2003; Jach *et al.*, 1999). Native oxide will be quickly sputtered away during irradiation and its effect on pattern formation is negligible. Silicon surface was irradiated at normal incidence angle with various ion doses. Dots were formed on the irradiated Si surface. Figure 7.1 shows one representative AFM image of surfaces sputtered with ion dose of 2.4×10^{18} ions/cm². The root-mean-square roughness of un-irradiated Si was 0.4 nm. Surface roughens after

ion beam irradiation, as shown in Figure 7.2. Roughness increases first and then drops for the range of ion dose studied (7.49×10^{16} ions/cm² to 2.4×10^{18} ions/cm²).

Figure 7.1 AFM images of Si (100) surface sputtered with 30 keV Ga⁺ ion beam at normal angle with ion dose of 2.4×10^{18} ions/cm².

The formation of dots at normal incidence angle is in agreement with usual expectation. However, it is in contrast with the results presented in Chapters 4 and 5, where well-developed ripples formed on Sn and Ti surfaces due to crystallographically-dependent anisotropic diffusion. It is well accepted that there is surface amorphization on semiconductors and ceramics after ion beam bombardment (Chini *et al.*, 2003; Jones and Santana, 1991; Nord *et al.*, 2002; Wang, 1998). The amorphization of Si surface upon ion bombardment induces dots formation.

Figure 7.2 RMS roughness as a function of sputtering time at normal angle (ion dose is 7.49×10^{16} ions/cm² for 1 min).

Gago *et al.* (2001; 2002) reported the production of ordered assemblies of silicon nanodots by the irradiation of a Si(100) substrate with 1.2 keV Ar⁺ ions at normal incidence. Atomic force image and high-resolution transmission electron microscopy showed that the silicon structures were crystalline, displayed homogeneous height, and spontaneously arranged into short-range hexagonal ordering. Regular nanostructure has important application in optoelectronic and quantum devices. Gago's report is the first one on producing nanodots on silicon surfaces at normal incidence irradiation. But the repeatability of Gago's experiments were not confirmed (Aziz, 2002).

In the present study, the dots are not ordered. They look more like random roughness.

Therefore, their formation may be regarded as “by-products” of the roughening and smoothing process during ion sputtering.

7.3 Rotated ripple structure at 30° incidence angle

Various off-normal incidence angles (15°, 30°, 45° and 60°) were used to study the effect of incidence angle on pattern formation. Ripples were formed easily at 30° incidence angle. However, no ripple was found at any other incidence angles (15°, 45° and 60°). Ripples formed at 30° incidence angle were carefully studied using AFM.

Figure 7.3 shows ripple formation with increasing ion dose. Ripple was formed at ion dose above 6.49×10^{16} ions/cm², as shown in Figures 7.3(a) and (b). Ripple orientation was perpendicular to projected ion beam direction as predicted by BH model (Figures 7.3(a) and (b)). When ion dose increased to 2.59×10^{17} ions/cm², ripples perpendicular to ion beam direction were vanishing, as shown in Figure 7.3(c). Ripple orientation was rotated when ion dose reached 5.19×10^{17} ions/cm², as shown in Figure 7.3(d). Rotated ripples were well developed with further increasing ion doses, as shown in Figures 7.3(e) and (f).

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Figure 7.3 Ripple formation and rotation at 30° incidence angle with increasing ion dose. (a) 6.49×10^{16} ions/cm²; (b) 1.30×10^{17} ions/cm²; (c) 2.59×10^{17} ions/cm²; (d) 5.19×10^{17} ions/cm²; (e) 1.04×10^{18} ions/cm²; (f) 1.95×10^{18} ions/cm². (dwell time for ion milling is 1 μ s)

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It is doubtful whether the orientation of rotated ripples is related to ion beam direction. Further experiments were carried out to study this. Figure 7.4 shows the relationship between ripple orientation and projected ion beam direction. When ion beam projection direction changes, ripple orientation changes correspondingly, as shown in Figures 7.4(a)-(f). That is to say, ripple orientation is neither perpendicular nor parallel to the projected ion beam direction but it is still dependent on the ion beam direction.

RMS roughness was investigated as a function of ion dose or sputtering time as shown in Figure 7.5. It is found that surface roughness increases linearly with ion dose studied.

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Figure 7.4 Ripple orientation vs projected ion beam direction and fast scan direction at 30° incidence angle and ion dose of 1.04×10^{18} ions/cm². (a) and (b) Original position; (c) and (d) Rotation of fast scan direction by 45°; (e) and (f) Rotation of fast scan direction by 90°. (dwell time for ion milling is 1 μ s)

Figure 7.5 RMS roughness as a function of ion dose (sputtering time) at 30° incidence angle. (dwell time for ion milling is 1 μ s)

Ripple formed on Si surface was observed by others at incidence angles other than 30° but they also used broad ion beam. Karmakar and Ghose (2004) investigated pattern formation on Si (100) irradiated with various incidence angles (10°-80°) with 16.7 keV broad Ar^+ ion at ion dose higher than 10^{17} ions/cm². They only observed ripple formation at the incidence angle of 60° and ripple orientation was perpendicular to the projected ion beam direction. Carter and Vishnyakov (1996) reported ripple production at 45° incidence angle on Si irradiated with 10–40 keV Xe^+ unfocused ion at temperatures between 100 and 300 K but no ripple for incidence angles of 0° to 40°. Ripple formation was also reported by Erlebacher *et al.* (1999) on Si (001) sputtered with

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750 eV Ar^+ ion (unfocused) at grazing incidence of 67.5° . O_2^+ sputtering of Si (100) surface at 40° incidence angle produced ripples for ion energies ranging from 1.5 to 9 keV (Vajo *et al.*, 1996). Ripple formed at incidence angles of 40° (Vajo *et al.*, 1996), 45° (Carter and Vishnyakov, 1996) and 60° (Karmakar and Ghose, 2004) was oriented perpendicular to the projected ion beam direction, while ripple orientation was parallel to the projected ion beam direction for larger incidence angle of 67.5° (Erlebacher *et al.*, 1999). It can be inferred that the difference in ion species and ion energy can account for the selection of optimal incidence angle for ripple formation.

Rotated ripple structure (RRS) was first predicted theoretically by Rost and Krug (1995), and later simulated numerically by Park *et al.* (1999). However, it should be noted that no ripple rotation was observed by other researchers.

For short erosion times, the ripple development and orientation follow the predictions of the linear BH model. However, after a well-defined crossover time, there is a clear separation of the linear and nonlinear behavior, and the surface morphology is determined by the nonlinear terms. When $\lambda_x \lambda_y > 0$ (λ_x and λ_y represent the tilt-dependent erosion rate, depending on ion flux J and the penetration depth a), the nonlinear terms destroy the ripple morphology and lead to rough phase governed by kinetic roughening. However, when $\lambda_x \lambda_y < 0$, they result in a long and apparently rough transient regime. After a crossover time, new ripples suddenly form and their direction is rotated with respect to the ion beam direction (Rost and Krug, 1995).

Kim *et al.* (2002) investigated the necessary conditions for the formation of RRSs and the impact of the various experimentally controllable parameters on the morphology of the RRS. They showed that at low temperatures the RRSs could form when the longitudinal width (σ) of the damage cascade generated by the ion beam was larger than the transverse width (μ) and the angle of the incident beam was chosen in a rather narrow window. By calculating the structure factor for RRS, it was found that RRS was more regular and their amplitude was more enhanced compared to the much studied ripple structure forming in the linear regime of sputter erosion.

Based on the experimental result on graphite surfaces, Habenicht *et al.* (2000) concluded that σ depended on the ion beam energy, while μ was independent of the ion beam energy for large energy (2-50 keV). It can be inferred that $\sigma > \mu$ can be met when the energy of the ion beam is high enough (Kim *et al.*, 2002). The ion energy used in the project is 30 keV, therefore it can meet the requirement for RRS formation.

While the presence of the RRS was proposed theoretically, the structure had not been observed experimentally before this finding. Our experiment testifies the existence of rotated ripple structures for the first time.

7.4 Effect of dwell time on ripple formation

Dwell time is the time the beam spends on a single pixel per pass. It is an important experimental parameter. Dwell time ranging from 0.1 to 600 μ s has been used to

investigate its effect on ripple formation. Table 7.1 listed the detailed experimental parameters.

Table 7.1 Parameters used to mill the $25 \times 20 \mu\text{m}^2$ area in Si (100)

Dwell time (μs)	Number of passes	Sputtering time (min:s)
0.1	5986	8:00
1	599	8:00
3	200	8:01
10	60	8:01
30	20	8:01
50	12	8:01
70	8	7:29
100	6	8:01
300	2	8:01
600	1	8:01

Figure 7.6 shows the effect of dwell time on pattern formation. For the shortest dwell time of $0.1 \mu\text{s}$, ripple was formed with orientation perpendicular to the projected ion beam direction (Figure 7.6(a)). The ripple wavelength is around $1.32 \mu\text{m}$. When dwell time was $1 \mu\text{s}$, rotated ripple was superimposed upon the ripple with orientation perpendicular to the projected ion beam direction, as shown in Figure 7.6(b). With dwell time increasing to $3 \mu\text{s}$, only ripple perpendicular to ion beam direction was present (Figure 7.6(c)). The ripple wavelength is $1.32 \mu\text{m}$, the same with that formed at dwell time of $0.1 \mu\text{s}$. Ridges were formed between ripples with wavelength of $1.32 \mu\text{m}$ when dwell time reached $10 \mu\text{s}$, as shown in Figure 7.6(d). Ripple disappeared and networks were formed on the irradiated surface for dwell time of $30 \mu\text{s}$, as shown in Figure 7.6(e). At dwell time of $50 \mu\text{s}$, ripple was formed again, as show in Figure 7.6(f).

However the ripple wavelength at 50 μs was 0.685 μm , half of those observed at dwell time of 0.1, 3 and 10 μs (Figures 7.6(a), (c) and (d)).

For short dwell time (0.1 and 1 μs) and longer dwell time (30 and 50 μs), incident ion beam projection direction and fast scan direction was rotated by 45° to see how pattern formation was affected by ion beam direction. After 45° rotation, ripples were formed at all dwell times studied with orientation perpendicular to the projected ion beam direction for the ion dose used, as shown in Figures 7.7(a)-(d). Ripple wavelength is 0.68 μm for all dwell times studied. It should be noted that surface morphology after ion beam rotation is different from that without rotation, *e.g.* Figure 7.6(b) compared with Figure 7.7(b), Figure 7.6(e) compared with Figure 7.7(c). Ripple wavelength after ion beam rotation is also different from that without rotation, such as Figure 7.6(a) compared with Figure 7.7(a).

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Figure 7.6 Effect of dwell time on pattern formation on Si (100) irradiated with 30° incidence angle. (a) 0.1 μs . (b) 1 μs . (c) 3 μs . (d) 10 μs . (e) 30 μs . (f) 50 μs . Crystallographic orientations are indicated in (b) and remain the same in other images.

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Figure 7.7 Pattern formation when ion beam fast scan direction and projection direction was rotated by 45° at various dwell times. (a) $0.1 \mu\text{s}$. (b) $1 \mu\text{s}$. (c) $30 \mu\text{s}$. (d) $50 \mu\text{s}$.

7.5 Effect of dwell time on sputtering yield

Sputtering depth under various dwell time was measured using AFM. Based on sputtering depth, sputtering yield was calculated. Sputtering depth and sputtering yield as a function of dwell time are shown in Figure 7.8. The sputtering yield remains constant at 3.7 atoms/ion till $100 \mu\text{s}$ dwell time and increases with further increase in dwell time, as shown in Figure 7.8. The increase in sputtering yield is attributed to edge-enhanced sputtering due to ejection of atoms from sidewall as well as from the top surface as discussed in the proposed model in Chapter 4.

Figure 7.8 Sputtering yield as a function of dwell time on Si surface (30° incidence angle and 5.19×10^{17} ions/cm²).

Table 7.2 Parameters set for SRIM MC simulations of Si (Ziegler, 2003)

Voltage (keV)	Incidence angle (°)	Surface binding energy (eV)	Lattice binding energy (eV)	Displacement energy (eV)	Density (g/cm ³)
30	30	4.7	2	15	2.321

SRIM MC simulation was used to simulate the interaction of Ga ions with Si substrate.

The parameters used for simulation are listed in Table 7.2. Sputtering yield from SRIM is 4 atoms/ion, close to with those under short dwell times obtained from experimental measurements. Figure 7.9 shows the damage cascade induced by Ga ions bombardment and ion trajectories in Si substrate.

Figure 7.9 SRIM MC simulations for 30 keV Ga^+ into Si at 30° incidence. (a) Damage cascade; (b) Ion trajectories in Si. The arrows indicate the incident directions of Ga^+ .

Surface roughness after ion irradiation was measured using AFM. Roughness as a function of dwell time is shown in Figure 7.10. There is no simple relationship between surface roughness and dwell time. Roughness reaches maxima at certain dwell times such as 1, 50 and 300 μs . Fast scan direction also influences the surface roughness. Roughness on surfaces irradiated with fast scan direction parallel to [110] is higher than that formed with fast scan direction parallel to [100] at the same dwell time.

Figure 7.10 RMS roughness as a function of dwell time. Open circle represents fast scan direction is parallel to [110]. Upward solid triangle represents fast scan direction is rotated 45° to be parallel to [100].

7.6 Effect of beam overlap on pattern formation

If not mentioned in the context, the beam overlap used in experiments is 50% in both X and Y directions. If overlap in one direction is decreased to negative value, it means that the adjacent spots are separated from each other in that direction. In the project, it was found that periodic structures (gratings) can be produced if negative overlap is used. The period of gratings is equal to the distance defined. Figure 7.11 shows fine gratings produced by decreasing beam overlap. The period of gratings as shown in Figure 7.11(d) is roughly equal to the beam distance defined (200nm).

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Figure 7.11 Fine gratings formed at 30° incidence angle, current of 100pA and overlap of -770% in Y direction (beam distance is 200nm). (a) SEM overall view. (b) SEM close-up of gratings. (c) AFM image of gratings. (d) AFM line profile showing grating period.

7.7 Summary

Dots were observed on surfaces irradiated at normal angle, but they are not ordered. Their formation may be regarded as “by-products” of the roughening and smoothening process during ion sputtering.

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Ripples were only observed on the irradiated surface at off-normal incidence angle of 30° . Ripple orientation was found to be rotated under larger ion doses (longer sputtering time). Rotation of ripple orientation was predicted theoretically, but the results obtained in the present study represent the very first experimental observation lending support to the theoretical model. Surface morphology is different under varying dwell time, but the ripple orientation is always dependent on the ion beam projection direction. It was also observed that sputtering yield increased with dwell time. This phenomenon is due to edge-enhanced sputtering at longer dwell time as predicted by the proposed new model in Chapter 4.

Fine gratings can be produced by increasing beam distance or changing beam overlap to negative value in one direction. Change of beam overlap demonstrates to be a viable method to control pattern formation.

Chapter 8 Pattern Formation on InP and GaAs Surfaces

Irradiated with Focused Ion Beam

8.1 Introduction

InP and GaAs are technologically important III-V semiconductors. InP (100) and GaAs (100) surfaces were irradiated with 30 keV Ga^+ ions using the focused ion beam machine. The surface morphology and roughness of irradiated area was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Energy dispersive x-ray spectroscopy (EDX) was used to carry out chemical microanalysis on the irradiated surfaces. Ripples were only observed on the irradiated InP surface at off-normal incidence angle of 30° . Surface roughness was much higher at incidence angle of 30° than at other incidence angles. In contrast to surface patterns on InP, only dots or islands were observed on GaAs surface for all the incidence angles used. The effect of dwell time on bitmap patterning shows that produced patterns can be well controlled under longer dwell time or larger feature size. Material redeposition can be easily observed on GaAs surface under higher ion doses or bitmap patterning condition. Adatom creation, transport and annihilation on GaAs surface have been firstly observed using *in situ* secondary electron imaging.

8.2 Pattern formation on InP (100)

InP is an important semiconductor used for optoelectronic and microwave devices. InP (100) surface was irradiated with 30 keV Ga^+ focused ion beam at various incidence

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angles (0° , 15° , 30° , 45° and 60°) to study the surface morphological evolution with increasing ion dose. It was found that ripple can only be formed at 30° incidence angle. Figure 8.1 shows the FIB imaging of surfaces irradiated with 30° incidence angle at various ion doses. The ripple orientation is perpendicular to the projected ion beam direction. Figure 8.2 shows corresponding AFM images at various ion doses. Insets shown in Figures 8.2(b), (c) and (d) display close-up images. AFM images clearly show that irradiated surfaces are decorated with nanodots with nominal diameter of about 100 nm. Ripples were also observed by Malherbe *et al.* (2005) on the InP (100) surfaces sputtered with 5 keV nitrogen ions at 41° incidence angle. Different experimental conditions might account for the discrepancy in optimal incidence angle for ripple formation.

Figure 8.3 shows the relationship between surface roughness and sputtering time at various incidence angles. It is seen clearly from the figure that surface roughens dramatically with ripple formation at 30° incidence angle. Surface roughness at 30° incidence angle increases with sputtering time and stabilizes at longer time. However for other incidence angles, such as 0° , 45° and 60° , roughness is not sensitive to the sputtering time and lower than surface irradiated at 30° incidence angle.

EDX spectra were collected for both origin surface and irradiated surfaces at excitation voltages of 20 kV and 15 kV. It was found that the atomic percentage of In was higher than that of P for irradiated InP surfaces. MacLaren *et al.* (1992) also reported that Ar^+ sputtering of InP led to surface enrichment of In that was accompanied by a change in In Auger line toward that for In metal. The mass difference between the In and P atoms is the major factor contributing to the preferential sputtering of P from InP surface, with

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the surface binding energies of secondary importance (Malherbe and Barnard, 1991). Yu *et al.* (1998) also observed significant P depletion on ion irradiated InP surface and attributed it to the combination of non-stoichiometric sputtering, ion bombardment induced Gibbsian surface segregation and enhanced diffusion.

Figure 8.1 FIB imaging of InP surfaces irradiated with varying ion dose at 30° incidence angle. (a) 2.59×10^{17} ions/cm². (b) 5.19×10^{17} ions/cm². (c) 1.04×10^{18} ions/cm². (d) 2.08×10^{18} ions/cm².

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Figure 8.2 AFM imaging of InP surfaces irradiated with varying ion dose at 30° incidence angle. (a) 2.59×10^{17} ions/cm². (b) 5.19×10^{17} ions/cm². (c) 1.04×10^{18} ions/cm². (d) 2.08×10^{18} ions/cm². Insets show close-up images.

Figure 8.3 RMS roughness on InP as a function of sputtering time

8.3 Pattern formation on GaAs (100)

GaAs is an important material for electronic and optical applications. Its characteristics under ion erosion have been systematically studied here.

When GaAs surface was irradiated with low ion doses at normal incidence, large dots were formed and distributed randomly on the irradiated area, as shown in Figures 8.4(a)-(c). Diameter of dots can be as large as 1.2 μm . The large dots were reduced in size or annihilated upon the arrival of more focused ions. With ion dose increasing, more and more materials were redeposited at the edge of the scanned area, as shown in Figures 8.4(d)-(f). Similar phenomena occurred to other incidence angles such as 15°, 30°, 45° and 60°.

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Figure 8.4 Pattern formation on GaAs (100) surfaces at normal incidence angle with increasing ion dose. (a) 7.49×10^{16} ions/cm². (b) 1.50×10^{17} ions/cm². (c) 3×10^{17} ions/cm². (d) 1.2×10^{18} ions/cm². (e) 2.4×10^{18} ions/cm². (f) 4.79×10^{18} ions/cm².

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Nanodots with circular shape in majority and angular shape in minority were observed on GaAs surfaces irradiated with larger incidence angles of 70° and 80°. Figure 8.5 and Figure 8.6 show AFM characterization of nanodots at 70° and 80° incidence angles respectively. In order to reveal the evolution of nanodot size with ion dose, nominal nanodot diameter was used. Software in Zeiss optical microscopy was used to measure the area and calculate nominal radius for each nanodot. Base on the data, average diameter of nanodots and standard deviation were calculated. Figure 8.7 shows that the average diameter of the nanodots is smaller at 80° incidence angle than that at 70° incidence angle. Diameter of nanodots decreases with ion dose for 80° incidence angle, as shown in Figure 8.7(b). For 70° incidence angle, the diameter of nanodots is a little higher at ion dose of 5.12×10^{16} ions/cm² (Figure 8.7(a)); however the overall trend is similar to that at 80° incidence angle. The experimental results are in agreement with those reported by Datta *et al.* (2002).

Datta *et al.* (2002) reported the formation of nanodots on GaAs bombarded by 60 keV broad Ar⁺ beam (current density of 25 μA/cm²) at room temperature with an incidence angle of 60°. The bombarded surface was populated by dots at ion dose below 1×10^{18} ions/cm². With increasing ion dose, the diameter was also found to decrease. Datta *et al.* (2002) also observed ripples at the dose of 3×10^{18} ions/cm². However ripple was not observed in our experiments on GaAs.

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Figure 8.5 AFM images showing nanodots formed on GaAs surfaces irradiated at 70° incidence angle with increasing ion dose. (a) 2.56×10^{16} ions/cm². (b) 5.12×10^{16} ions/cm². (c) 1.02×10^{17} ions/cm². (d) 2.05×10^{17} ions/cm².

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Figure 8.6 AFM images showing nanodots formed on GaAs surfaces irradiated at 80° incidence angle with increasing ion dose. (a) 1.3×10^{16} ions/cm². (b) 2.6×10^{16} ions/cm². (c) 5.2×10^{16} ions/cm². (d) 1.04×10^{17} ions/cm².

Figure 8.7 Histogram showing average dot diameter as a function of ion dose at various incidence angles. (a) 70°. (b) 80°.

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For the lowest dose level (2.56×10^{16} ions/cm²) studied at 70° incidence angle, no material removal was observed. The rastered surface “swelled” above the original GaAs surface level by a few tens of nanometers (Figures 8.8(a) and (b)). Similarly, the rastered surface also “swelled” above the original GaAs surface level by a few tens of nanometers for the lowest dose level (1.3×10^{16} ions/cm²) studied at 80° incidence angle, as shown in Figures 8.9(a) and (b).

Zhou *et al.* (2003) reported swelling of FIB irradiated surface on Ge at ion dose below 5.2×10^{16} ions/cm². This surface swelling may be a result of the gallium ion implantation effect (Frey *et al.*, 2003), but also of the generation of damages modifying locally the parameters of the highly crystalline target (Lugstein *et al.*, 2002). Voids and interstitial atoms are created during ion bombardment leading to a local volume expansion (Gierak *et al.*, 2005; Schmuki *et al.*, 1997).

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Figure 8.8 (a) AFM image at dose of 2.56×10^{16} ions/cm² and incidence angle of 70°. (b) AFM line profile showing that part of the rastered surface swelled above the original GaAs surface.

Figure 8.9 (a) AFM image at dose of 1.3×10^{16} ions/cm² and incidence angle of 80°. (b) AFM line profile showing that part of the rastered surface swelled above the original GaAs surface.

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It is interesting to note that nanodots were also formed at the “original surface” close to the predefined irradiation area. As seen from Figure 8.10, both density and size of the nanodots decreased with the distance away from the predefined area. The result can possibly be explained by the Gaussian distribution of ion beam intensity. At the rim of exposed area, where beam tails hit the sample, a much lower fluence reached the surface and caused formation and distribution of nanodots (Frey *et al.*, 2003). Scattering of redeposited materials might also contribute to the formation and evolution of nanodots at the areas close to the predefined irradiation area.

Figure 8.10 AFM images showing nanodots formation on the area of GaAs close to the defined irradiation area with various ion doses. (a) and (b) 2.56×10^{16} ions/cm². (c) 2.05×10^{17} ions/cm².

8.4 Droplet formation on GaAs (100)

A serious and deleterious complication to micromachining is redeposition. As material is sputtered away, some of it becomes redeposited in the area that is being sputtered. In normal mechanical machining, build-up of machined material is avoided by the use of liquid or air streams that carry the swarf away. In FIB machining redeposition is critically dependent upon how the milling is performed. It has been shown that for the same total dose, scans that are repeated many times to mill an area cause less deposition to occur than a single slow pass to mill the rectangular. For the slow scan, redeposited material is not removed, whereas for the fast repeated scans, some fraction of the primary beam is used to sputter away redeposited material (Orloff et al., 2003; Yamaguchi et al., 1985).

8.4.1 Effect of dwell time on bitmap patterning

Quanta 3D FIB is implemented with a digital patterning generator that allows for complete FIB milling by utilizing direct import of bitmap files. The data of bitmap file is stored as pixels. The dwell time for each pixel can be defined uniquely. The dwell time of each pixel of the ion beam location is normalized to the grayscale value (or color value) so that white is the longest dwell time and black is zero dwell time; a region where no milling occurs. The milling depth or deposition height may be specified by defining the number of scanned beam passes within the given structure.

The process of translating the bitmap to a milled pattern is as follows:

1. User loads bitmap onto screen;
2. Bitmap can be resized and the maximum dwell time is set;

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3. When it comes time to mill the pattern each pixel in the bitmap is read and translated into an x, y & dwell time ready for downloading to the patterning board;

4. If the pixel is a non-milling one then it is ignored;

5. If the pixel is to be milled then a dwell time is calculated based on the maximum dwell time set up for the pattern and the blue value of the bitmap pixel. There is a table of 124 dwell times in the range 100 ns to 4.6 ms. The distribution is logarithmic so that the step from one dwell time to the next is a similar fractional size. The requested dwell time is then looked up in the 124 entry dwell table to determine the dwell index to download to the pattern board.

Bitmap files can be made using Excel, Matlab, AutoCAD or Photoshop. The bitmap file of square-shaped pattern as shown in Figure 8.11 was used as input file for the Quanta 3D FIB system. The use of low beam currents is essential to achieve a good fabrication quality using FIB. Ion beam current of 30 pA (16 nm in beam diameter) and normal incidence angle were used in all FIB bitmap patterning. In addition to beam current, dwell time and scan size are important parameters to control the milling quality.

Two kinds of scan area were used: $10 \times 10 \mu\text{m}^2$ and $20 \times 20 \mu\text{m}^2$, with corresponding defined feature sizes as 160 nm and 320 nm. Figure 8.12 and Figure 8.13 show pattern formation on scan area of $20 \times 20 \mu\text{m}^2$ milled by FIB for fixed sputtering time of 4 min at various dwell times. Figure 8.14 and Figure 8.15 show pattern formation on scan area of $10 \times 10 \mu\text{m}^2$ milled by FIB for fixed sputtering time of 4 min at various dwell times.

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Figure 8.11 Bitmap file used to mill the 3D structures. Distance between two nearest squares is equal to the length of the square.

Figure 8.12 AFM image showing pillar formation on GaAs by FIB bitmap patterning under dwell time of 100 μ s (defined feature size of 320 nm).

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Figure 8.13 Bitmap patterning of GaAs under varying dwell time and fixed sputtering time of 4 min (defined feature size of 320 nm). (a) 0.1 μ s. (2) 0.2 μ s. (3) 0.3 μ s. (d) 0.5 μ s. (e) 1 μ s. (f) 3 μ s.

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The AFM image in Figure 8.12 shows the well-controlled patterns on GaAs surface in terms of shape and period using the bitmap file as defined in Figure 8.11. However, the pattern quality will be deteriorated by decreasing the dwell time. For the shortest dwell time (0.1 μs), patterns are connected with each other in FIB fast scan direction and displayed as “gratings”, as shown in Figure 8.13(a). With dwell time increasing, patterns are separated from each other and shape of pattern evolves from rectangular to square, as shown in Figures 8.13(b)-(e). When dwell time is increased to 3 μs , the patterns produced are the same as defined, as shown in Figure 8.13(f). The results show that longer dwell time is beneficial to get user-defined patterns for this material.

When bitmap size is decreased to $10 \times 10 \mu\text{m}^2$, the defined feature size is 160 nm. Pattered features at lowest dwell time are also connected with each other in fast scan direction, as shown in Figure 8.14(a) and Figure 8.15(a). With dwell time increasing, the discrete features are formed, as shown in Figures 8.14(b)-(d). However, the features have a conical shape, corners of the pillars are rounded shapes, indicating a reduced patterning quality (Figure 8.15(b)). Furthermore, a large amount of redeposited material is observed on the sputtered surface. The chemical analysis of redeposited droplets and cause for it are further discussed in next section.

Figure 8.16 show the relationship between sputtering depth of features and dwell time. It is seen from the figure that sputtering depth increases with dwell time initially but saturates after dwell time is over 3 μs .

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Figure 8.14 SEM images showing bitmap patterning of GaAs surface under various dwell times and fixed sputtering time of 4 min (defined feature size of 160 nm). (a) 0.1 μ s. (b) 3 μ s. (c) 30 μ s. (d) 100 μ s.

Figure 8.15 AFM images showing bitmap patterning of GaAs surface under fixed sputtering time of 4 min (defined feature size of 160 nm) and dwell time of (a) 0.1 μ s and (b) 30 μ s.

Figure 8.16 Sputtering depth as a function of dwell time with defined feature size of 320 nm.

8.4.2 Chemical analysis of sputtered surface

In order to determine the chemical composition of liquid-like droplets redeposited on the patterned GaAs surfaces, EDX was used. Incident electron beam voltage used in EDX affects the interaction volume between beam and material. A numerical expression (Kanaya & Okayama, 1972) to estimate the radial range of electron interaction volume is:

$$R (\mu m) = \frac{0.0276}{\rho Z^{0.89}} A E_o^{1.07} \cos(\theta) \quad (8-1)$$

where A is the atomic weight (g/mol), Z is the atomic number, ρ is the density (g/cm³), E_o is the electron beam voltage (keV) and θ is the angle with respect to the surface normal.

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The volume of interaction can be modeled by Monte Carlo simulation. In such models, the likelihood of incident electrons interacting with the sample and scattering and the angle of deflection are determined probabilistically. CASINO (Monte Carlo Simulation of Trajectory in Solids) Version 2.42 free online software was used to investigate the interaction of electron beam with a Ga substrate at various accelerating voltages. 2000 electrons were used in the simulation. Simulation shows that the depth of electron penetration and size of excitation volume increase with electron voltage, as shown in Figure 8.17. Electron voltage also influences the relationship between intensity of characteristic x-rays and sample depth. CASINO simulates x-ray intensity of non-absorbed Ga L as a function of depth at various beam voltages as shown in Figure 8.18. X-ray generation depths depend strongly on accelerating voltage. Lower voltage can only excite characteristic x-rays from shallower surface.

For the same droplet redeposited on patterned GaAs surface, EDX spectra were collected at different beam voltages, as shown in Figure 8.19, to reveal the elemental composition of droplets redeposited. It is clear that the atomic percentage of Ga increases with decreasing excitation voltage. At beam voltage of 5 keV, the droplet contains 100% Ga. According to the relationship of x-ray intensity with depth at varying voltages shown in Figure 8.18, the depth of Ga droplet can be estimated to be 170 nm. The irradiated area without obvious redeposition was also shown to be Ga enriched according to quantitative EDX analysis. The average atomic ratio of Ga to As is 1.33 at 5 keV excitation voltage.

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Figure 8.17 Monte Carlo simulation excitation volumes of electron beam at varying voltage with Ga substrate.

Figure 8.18 X-ray intensity of non-absorbed Ga L as a function of depth at various beam voltages.

Figure 8.19 EDX spectra from droplet redeposited on the irradiated GaAs surface under varying excitation electron voltage.

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Lugstein *et al.* (2004b) analyzed the composition of the dots on GaAs surface after FIB processing using AES spectra and found that the dots were Ga-rich agglomerates and metallic Ga after RTA. Due to the excess Ga atoms, produced by preferential sputtering and because of enhanced diffusion, the Ga atoms agglomerate into the observed Ga-rich precipitates.

It is generally accepted that the FIB irradiation leads to decomposition of GaAs. The often invoked mass-dependent models (Haff, 1977; Ho *et al.*, 1979) predict that the lighter atomic species are preferentially sputtered away, thus the surface is enriched in the heavier species. In the case of GaAs, the mass difference between Ga and As is negligibly small and the difference in the surface binding energies plays the dominant role in the preferential sputtering of GaAs. The sublimation energy is usually taken to represent the surface binding energy of an atomic species (Sigmund, 1980). A comparison of the sublimation energies shows that the sublimation energy of As ($H_s(\text{As}) = 29 \text{ kcal mol}^{-1}$) is smaller than that of Ga ($H_s(\text{Ga}) = 64.9 \text{ kcal mol}^{-1}$) (Pan *et al.*, 1997; Singer *et al.*, 1981). Therefore As is preferentially sputtered from GaAs and leave surface Ga enrichment.

During ion bombardment of GaAs, the preferential sputtering of As from GaAs causes Ga enrichment in the surface region. Then surface diffusion and agglomeration lead to the development of Ga islands. These islands then seed the development of sputter cones through the higher sputtering yield of GaAs than that of Ga. The preferential sputtering of As decreases as the As concentration of surface region decreases. On the other hand, the irradiation-enhanced diffusion helps to increase the As surface concentration. According to the conservation principle, the equilibrium sputtered

surface composition is finally reached when the partial sputtering yield of As is equal to that of Ga from GaAs. The actual As concentration on the surface will be governed by an interplay between preferential sputtering and ion irradiation enhanced diffusion processes.

In addition to decomposition and preferential sputtering, Ga implantation may play an important role in the formation of metallic Ga droplets. When implanted Ga exceeds the solubility limit of the host material GaAs under high ion dose, Ga atoms may tend to diffuse to the surface and segregate. Thus Ga droplet forms. EDS and AES characterization of FIB irradiated Si surface (Pellerin *et al.*, 1989) revealed that Ga incorporation into Si could be as high as 38 at.%. Although the authors showed significant chemical modification to the substrate caused by Ga ion beam, they did not reported the effect of implantation on surface morphology. A recent study by Buckmaster *et al.* (2005) observed that metallic Ga nanodots formed on the SiO₂ surface for ion dose above a critical value, while Ga nanodots nucleated just below the surface for low ion dose. The study lends further support to the statement that the formation of Ga droplets is related to diffusion and segregation of supersaturated Ga.

8.4.3 Adatom diffusion and annihilation on sputtered surface

When feature size defined in bitmap file is small, it is very easy to get material redeposited on irradiated surface. In order to gain detailed information about the redeposition process, the same experimental parameters except sputtering time as that used in Figure 8.14 were used to repeat the whole process. SEM image was taken every 20 s of ion irradiation time to record the surface morphology of irradiated surface.

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Figure 8.20 shows selected SEM images taken in the irradiation process to reveal the evolution of pattern formation and material redeposition. Arrow 1 and arrow 2 are used to guide the eyes. After GaAs surface is irradiated for 120 s, material redeposition can be obviously observed, as shown in Figure 8.20(a). Deposited material grows, saturates and transports to other positions as indicated by arrows 1 and 2 in Figure 8.20.

Mass transport phenomena can be directly observed on GaAs using *in situ* secondary electron imaging. Figure 8.21 shows the nucleation and growth of adatom islands during initial irradiation stage. Shortly after 13 seconds ion irradiation (ion dose of 2×10^{16} ions/cm²), nuclei were observed as shown in Figure 8.21(b). Then those nuclei with dimension larger than critical nuclei diameter grew larger and larger, as shown in Figures 8.21(c)-(f). The density of nanodots and average diameter do not vary with sputtering time after initial stage. Figure 8.22 shows adatom diffusion and annihilation process under longer sputtering time (ion dose).

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Figure 8.20 SEM images showing time evolution of material redeposition and surface diffusion on GaAs. (a) 120 s. (b) 140 s. (c) 160 s. (d) 180 s. (e) 200 s. (f) 220 s. Arrows 1 and 2 guide the eyes to changes.

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Figure 8.22 *In situ* imaging of GaAs surfaces irradiated with 100 pA and 30 kV at normal angle and at various sputtering times showing adatom diffusion and annihilation. Ellipses labeled with 1, 2 and 3 draw attention to evolution of islands inside. (a) 06:42. (b) 06:48. (c) 06:51. (d) 06:53.

The dot formation at different ion currents shows similar evolution process, but the density of dots increases as a function of ion current. Typical histograms of size distribution of dots at 100 pA and 30 pA are shown in Figure 8.23 and Figure 8.24 respectively. The size distribution of dots is much narrower and average dot diameter is smaller at higher current.

Figure 8.23 Histogram showing the size distribution of dots at an ion dose of 6.37×10^{17} ions/cm² at 100 pA.

Figure 8.24 Histogram showing the size distribution of dots at an ion dose of 5.55×10^{16} ions/cm² at 30 pA.

The nanodots are composed of adatom clusters and mobile. Some of them coalesce into larger nanodots during transport, as shown in ellipses 1 and 2 in Figure 8.22. Some others are annihilated by traps such as step edges or surface vacancies or they are directly removed by impinging ions, as shown in ellipse 3 in Figure 8.22. The whole process is schematically shown in Figure 8.25.

Figure 8.25 Schematic image showing the process of adatom creation, diffusion and annihilation.

The concentration of surface adatoms $C(r,t)$ (Erlebacher *et al.*, 1999; Li *et al.*, 2001) is governed by a two-dimensional diffusion equation:

$$\frac{\partial C(r,t)}{\partial t} = JY_1 - JC\sigma_c - \frac{C}{\tau_1} - \frac{2C^2}{\tau_2} \quad (8-2)$$

where r and t are surface position and time. J is incident ion flux. Y_1 is the number of adatoms created per incident ion. Cross section σ_c is related to the area at the surface over which an ion's damage is deposited in the collision cascade. τ_1 is the characteristic time for an adatoms to diffuse to vacancy or other surface trap, and τ_2 is the characteristic time for two adatoms to impinge.

The influence of ion bombardment on the energetics or kinetics governing atomic transport has been used to produce single-digit nanopores for DNA sequencing. Li *et al.* (2001) used low-energy ion beam to irradiate a prepatterned pore and observed the

pore-closing phenomenon. A lateral atomic flow of matter into the pore stimulated by the ion beam can account for the closure of pores. Here the mass transport under ion bombardment has been firstly “seen” on GaAs surfaces using FIB imaging in-situ.

8.5 Summary

Focused Ga ion sputtering of compound semiconductors InP (100) and GaAs (100) has been investigated using SEM, FIB imaging and AFM. Ripples were formed on InP only at 30° incidence angle. The surface roughness at 30° incidence angle increases with ion dose and is much higher than those at other incidence angles. GaAs surface displays a different morphology under ion erosion. Nanodots were formed on irradiated GaAs surface. Diameter of nanodots decreases with incidence angle and ion doses. Materials redeposition is very obvious under higher ion dose and smaller defined feature size in imported bitmap files. Longer dwell time and larger defined feature size are beneficial to produce well-controlled patterns. Adatoms created by ion bombardment have been observed to nucleate and grow during initial stage. The process of adatom diffusion, coalescence and annihilation were also observed for the first time on irradiated GaAs surface using *in situ* secondary electron imaging.

There is preferential sputtering occurring to the compound semiconductors. In case of InP, phosphorus is preferentially sputtered due to lighter mass compared with indium. While regarding GaAs, arsenic is preferentially sputtered due to smaller sublimation energy. Both the preferential sputtering of As and supersaturation of Ga account for the formation of metallic Ga droplets.

Chapter 9 Conclusions and Future Work

9.1 Conclusions

Pattern formation has been investigated on different materials using various FIB incidence angles (0° , 15° , 30° , 45° , 60° , 70° and 80°) over a wide range of ion doses (10^{16} - 10^{18} ions/cm²). Ripples were observed on metals (Sn and Ti) at both normal incidence angle and oblique incidence angles due to crystallographically-dependent anisotropic surface diffusion. Because of surface amorphization upon ion bombardment, ripples on ZnO and semiconductors (Si and InP) formed only at oblique incidence angles. The formation of metallic Ga dots on irradiated GaAs surface is mainly attributed to supersaturation of implanted Ga ions. There are preferable incidence angles for ripple formation, *e.g.*, 45° and 60° on ZnO, 30° on Si and InP. Investigations on Sn and Si show that sputtering yield increases with dwell time in general, which is attributed to edge-enhanced sputtering at longer dwell times. Conclusions are made in terms of type of material in the following sections.

9.1.1 Pattern formation on metals irradiated with FIB

Ripples formed on Sn and Ti surfaces at room temperature at both normal and off-normal incidence angles. The orientation of ripples depended on crystallographic orientation rather than the ion beam direction.

Quantitative analysis of irradiated Sn surface shows that the ripple amplitude increased with ion dose. The ripple wavelength was independent of ion dose for short dwell time (3 μs), but increased with ion dose first and stabilized under larger ion dose for long dwell time (15 μs).

Dwell time was used to tune surface morphology on Sn surface. Two kinds of characteristic ripples were observed over a large range of dwell time varying from 0.1 μs to 100 μs at 30° incidence angle. One kind of ripples with wavelength of 540 nm was found for short dwell-times (0.1 to 2 μs) and the other kind of ripples with wavelength of 1.7 μm was observed for long dwell-times (3 to 20 μs). Orientation is different for the two kinds of ripples.

The sputtering yield increases with dwell time significantly on Sn surface. A model is proposed to explain the interesting observation and attributes the increased sputtering yield under longer dwell time to ejection of atoms from the sidewall. The sputtering yield at short dwell time tallies with Monte Carlo simulation by SRIM.

It is proposed that the ripple formation on metals can be explained by the interplay between curvature-dependent ion erosion and crystallographically-dependent anisotropic surface diffusion. The competition between these two factors is determined by characteristics of metals. For low-melting-point metal Sn, ripples formed only in diffusive regime. However, for high-melting-point metal Ti, curved ripples or

fragmented rods viewed from different angles were observed at larger incidence angles and it is due to progressively increased influence by erosive regime.

9.1.2 Pattern formation on ZnO irradiated with FIB

Ripples formed on ZnO thin films only at 45° and 60° FIB incidence angles. Ripple orientation was always perpendicular to the projected ion beam direction. Both ripple wavelength and surface roughness increased with sputtering time (ion dose). The ripple formation on thin films can be explained by inclusion of Ehrlich-Schwoebel barrier in the well-accepted BH model.

9.1.3 Pattern formation on semiconductors irradiated with FIB

In contrast to results on metals, no ripple was observed on Si (100), InP (100) and GaAs (100) surfaces at normal incidence angle. Ripples formed on Si and InP surfaces at 30° incidence angle only. Ripple orientation was perpendicular to projected ion beam direction. It was found that ripple formed on InP was actually covered with large quantity of nanodots. Only dots or islands were observed on GaAs (100) surface for the wide range of incidence angles used. Diameter of nanodots on GaAs decreased with incidence angle and ion doses. Preferential sputtering was observed on compound semiconductors: P from InP and As from GaAs. Diffusion of supersaturated Ga may account for the formation of metallic Ga droplets.

It is very interesting to observe ripple rotation on Si surface under prolonged ion dose. Rotation of ripples was predicted theoretically, but the results obtained in the current project represent the very first experimental observation to support the theoretical model.

Dwell time can also tune surface morphology on Si surface, but ripple formed was always oriented perpendicular to the ion beam projection direction. Similar to the results on Sn surface, sputtering yield was also observed to increase with dwell time on Si surface. It indicates that the proposed new model in Chapter 4 taking into account edge effect can be extended to other material systems to explain the increase of sputtering yield under longer dwell time.

Material redeposition was clearly observed on areas close to the irradiated GaAs area. Swelling above the original surface was observed under low ion doses. Bitmap patterning facilitates the observation of redeposited droplets on GaAs surface under higher ion doses. EDX analysis shows that deposited droplets are pure Ga. The depth of Ga droplets is as high as 170 nm as indicated by CASINO. Evolution of surface morphology was recorded using *in situ* secondary electron imaging. It is very interesting to observe the process of adatom creation, diffusion, coalescence and annihilation on GaAs surface for the first time using this special function provided by the new FEI FIB system.

Change of beam overlap and bitmap patterning are demonstrated to be viable methods

for producing periodic nanoscale patterns. It is shown that longer dwell time or larger feature size can produce well defined nanoscale structures.

9.2 Future Work

- (1) Crystallographic orientation has great effect on ripple formation and its direction on irradiated metal surfaces; however, the clear relationship for certain material is not yet fully understood. EBSD (electron backscatter diffraction) will be used to detect crystallographic orientation to make it possible to determine the quantitative relationship between ripple direction and crystallographic orientation.
- (2) Further experiments will be carried out to explore the crossover time when surface morphology transits to a rotated ripple structure and window of operation parameters for rotated ripple formation.
- (3) Bombarded surfaces will be analysed using TEM to reveal microstructures or nanostructures after ion irradiation. Investigation of ion-induced damage by TEM will provide input to the theoretical studies on the mechanism of ripple growth, as well as to elucidate the basic mechanism of ion-solid interaction.
- (4) No model can possibly explain why certain incidence angles are preferable than others for pattern formation on a certain material. Theoretical analysis and

modeling will be further developed to have a fuller understanding of the mechanism.

- (5) The self-organized structures are thermodynamically stable, but lack of external controllability and lack of pattern regularity are the potential problems with the approach. Further researches will address the problems by exploring the possibility of producing nanoscale ripples or dots with good periodicity through “controlled self-organization”, which may be achieved by templating the surface or by adjusting the tempo-spatial distribution of FIB spots.
- (6) Self-assembled nanostructures such as nanodots, nanowires, nanorods, nanobelts, and nanotubes have attracted a great deal of attention for use in various applications including nanoscale optical devices, field emitters, nanoscale circuits, and nanosensors. However, in spite of a number of reports on the fabrication of self-assembled nanostructures, one of the major obstacles to achieving nanostructure-building blocks is the ability to control nanostructures with a desired size and forming position in the synthesis process. Pure Ga droplets on nanoscale formed on FIB irradiated GaAs surfaces present a promising method regarding this (Lugstein *et al.*, 2004a & 2004b & 2004c). The correlation between size and shape of droplets and experimental variables needs to be explored further. The well-controlled periodicity, size and position of Ga droplets will be of significance to produce size- and position-manipulated nanostructures. Ga droplets might also act as catalysts in the growth of semiconductor nanowires

Chapter 9 Conclusions and Future Work

(Aziz, 2005) during chemical vapor deposition (CVD) or physical vapor deposition (PVD). Method of producing pure metal droplets is also promising to be extended to other material systems.

Publications

W. Zhou, H. X. Qian and L. M. Wang, Maskless Fabrication of Highly-Ordered Periodic Nanopillars using FIB and Bitmap Control, *Microscopy and Microanalysis*, Cambridge Univ Press, UK, 2005, Vol. 11, S2, pp. 822-823.

H. X. Qian, W. Zhou, H. Y. Zheng, G. C. Lim, Morphological and Chemical Evolution on InP(100) Surface Irradiated with Femtosecond Laser, *Surface Science*, 2005, Vol. 595, pp.49-55.

H. X. Qian, W. Zhou and H. Y. Zheng, Ripple Formation on InP surface Irradiated with Femtosecond Laser, *International Journal of Nanoscience*, 2005, Vol. 4, No. 4, pp. 779-784

Y. Q. Fu, H. X. Qian, B. K. A. Ngoi and W. Zhou, Investigation of Thermal Effect of Microstructures Fabricated via Focused Ion Beam Raster Scanning, *International Journal of Nanoscience*, 2005, Vol. 4, No. 4, pp. 537-541.

H. X. Qian, W. Zhou, Y. Q. Fu, B. K. A. Ngoi and G. C. Lim, Crystallographically-dependent Ripple Formation on Sn Surface Irradiated with Focused Ion Beam, *Applied Surface Science*, 2005, Vol. 240, Nos. 1-4, pp. 140-145.

H. Y. Zheng, W. Zhou, H. X. Qian, T. T. Tan and G. C. Lim, Polarisation-Independence of Femtosecond Laser Machining of Fused Silica, *Applied Surface Science*, 2004, Vol. 236, Nos. 1-4, pp. 114-119.

References

- Ataev, B. M., Kamilov, I. K. and Mamedov, V. V. (1997). Zinc oxide whiskers. *Technical Physics Letters* 23, 842-843.
- Aziz, M. J. (2002). Private communications.
- Aziz, M. J. (2005). Private communications.
- Barabási, A. L. and Stanley, H. E. (1995). Fractal concepts in surface growth. Cambridge, Cambridge University Press.
- Bauccio, M., Ed. (1993). ASM Metals Reference Book, Third Edition, ASM International.
- Behrisch, R. and Wittmaack, K., Eds. (1991). Sputtering by particle bombardment III. Heidelberg, Springer-Verlag.
- Bevolo, A. J. (1989). Ion/Solid Interactions in Surface Analysis. Characterization of Semiconductor Materials - Principles and Methods. G. E. McGuire (Ed.). New Jersey, Noyes/William Andrew Publishing.
- Biersack, J. P. and Haggmark, L. G. (1980). A Monte Carlo computer program for the transport of energetic ions in amorphous targets. *Nuclear Instruments and Methods* 174, 257-269.
- Bischoff, L., Teichert, J. and Hausmann, S. (2001). Dwell-time dependence of irradiation damage in silicon. *Nuclear Instruments and Methods in Physics Research Section B* 178, 165-169.
- Bobek, T., Facsko, S., Dekorsy, T. and Kurz, H. (2001). Ordered quantum dot formation on GaSb surfaces during ion sputtering. *Nuclear Instruments and Methods in Physics Research Section B* 178, 101-104.

References

- Bradley, R. M. and Cirlin, E.-H. (1996). Theory of improved resolution in depth profiling with sample rotation. *Applied Physics Letters* 68, 3722-3724.
- Bradley, R. M. and Harper, J. M. E. (1988). Theory of ripple topography induced by ion bombardment. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 6, 2390-2395.
- Buckmaster, R., Hanada, T., Kawazoe, Y., Cho, M.-W., Yao, T., Urushihara, N. and Yamamoto, A. (2005). Novel method for site-controlled surface nanodot fabrication by ion beam synthesis. *Nano Letters* 5, 771-776.
- Burmer, C., Gorlich, S. and Pauthner, S. (1998). Application of layout overlay for failure analysis. *Microelectronic Reliability* 38, 987-992.
- Carter, G. (1997). Theory of ripple topography inhibition in depth profiling with sample rocking. *Applied Physics Letters* 71, 3066-3068.
- Carter, G. (1999). The effects of surface ripples on sputtering erosion rates and secondary ion emission yields. *Journal of Applied Physics* 85, 455-459.
- Carter, G. (2001). The physics and applications of ion beam erosion. *Journal of Physics D: Applied Physics* 34, R1-R22.
- Carter, G. and Vishnyakov, V. (1996). Roughening and ripple instabilities on ion-bombarded Si. *Physical Review B* 54, 17647-17653.
- Chan, W. L., Pavenayotin, N. and Chason, E. (2004). Kinetics of ion-induced ripple formation on Cu(001) surfaces. *Physical Review B (Condensed Matter and Materials Physics)* 69, 245413-6.
- Chason, E. and Aziz, M. J. (2003). Spontaneous formation of patterns on sputtered surfaces. *Scripta Materialia* 49, 953-959.

References

- Chason, E., Erlebacher, J., Aziz, M. J., Floro, J. A. and Sinclair, M. B. (2001). Dynamics of pattern formation during low-energy ion bombardment of Si(001). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 178, 55-61.
- Chaudhari, P., Lacey, J., Doyle, J. and Galligan, E. (2001). Atomic-beam alignment of inorganic materials for liquid-crystal displays. *Nature* 411, 56-59.
- Chen, W. (1994). Ga⁺ focused ion beam processing of gallium arsenide and silicon. Ph.D. thesis, University of Southern California.
- Chen, Y. J., Wang, J. P., Soo, E. W., Wu, L. and Chong, T. C. (2002). Periodic magnetic nanostructures on self-assembled surfaces by ion beam bombardment. *Journal of Applied Physics* 91, 7323-7325.
- Chen, Z., Shan, Z., Li, S., Liang, C. B. and Mao, S. X. (2004). A novel and simple growth route towards ultra-fine ZnO nanowires. *Journal of Crystal Growth* 265, 482-486.
- Chini, T. K., Okuyama, F., Tanemura, M. and Nordlund, K. (2003). Structural investigation of keV Ar-ion-induced surface ripples in Si by cross-sectional transmission electron microscopy. *Physical Review B* 67, 205403.
- Chini, T. K., Sanyal, M. K. and Bhattacharyya, S. R. (2002). Energy-dependent wavelength of the ion-induced nanoscale ripple. *Physical Review B* 66, 153404-1-4.
- Chiou, W.-T., Wu, W.-Y. and Ting, J.-M. (2003). Growth of single crystal ZnO nanowires using sputter deposition. *Diamond and Related Materials* 12, 1841-1844.
- Costantini, G., Rusponi, S., Gianotti, R., Boragno, C. and Valbusa, U. (1998). Temperature evolution of nanostructures induced by Ar⁺ sputtering on Ag(001). *Surface Science* 416, 245-254.
- Costantini, G., Rusponi, S., Mongeot, F. B. d., Boragno, C. and Valbusa, U. (2001). Periodic structures induced by normal-incidence sputtering on Ag(110) and Ag(001):

flux and temperature dependence. *Journal of Physics: Condensed Matter* 13, 5875-5891.

Goswami, D. K., Dev, B. N. (2003). Observation of smoothing and self-affine fractal roughness on MeV ion-irradiated Si surfaces. *Nuclear Instruments and Methods in Physics Research B* 212, 253-257.

Cuenat, A. and Aziz, M. J. (2002). Spontaneous Pattern Formation from Focused and Unfocused Ion Beam Irradiation. *Mat. Res. Soc. Symp. Proc.* 696, N2.8.1-N2.8.6.

Cuerno, R. and Barabási, A.-L. (1995). Dynamic Scaling of Ion-Sputtered Surfaces. *Physical Review Letters* 74, 4746-4749.

Datta, D., Bhattacharyya, S. R., Chini, T. K. and Sanyal, M. K. (2002). Evolution of surface morphology of ion sputtered GaAs(100). *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 193, 596-602.

Davies, S. T. and Khamsehpour, B. (1993). End-point detection using absorbed current, secondary electron, and secondary ion signals during milling of multilayer structures by focused ion beam. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 11, 263-267.

Dijken, S. v., Bruin, D. d. and Poelsema, B. (2001). Kinetic Physical Etching for Versatile Novel Design of Well Ordered Self-Affine Nanogrooves. *Physical Review Letters* 86, 4608-4611.

Ecke, G., Kosiba, R., Kharlamov, V., Trushin, Y. and Pezoldt, J. (2002). The estimation of sputtering yields for SiC and Si. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 196, 39-50.

Ehrlich, G. and Hudda, F. G. (1966). *Journal of Chemical Physics* 44, 1039.

References

- Erlebacher, J., Aziz, M. J., Chason, E., Sinclair, M. B. and Floro, J. A. (1999). Spontaneous Pattern Formation on Ion Bombarded Si(001). *Physical Review Letters* 82, 2330-2333.
- Erlebacher, J., Aziz, M. J., Chason, E., Sinclair, M. B. and Floro, J. A. (2000). Nonlinear amplitude evolution during spontaneous patterning of ion-bombarded Si(001). *Journal of Vacuum and Science Technology A* 18, 115-120.
- Facsko, S., Dekorsy, T., Koerdt, C., Trappe, C., Kurz, H., Vogt, A. and Hartnagel, H. L. (1999). Formation of ordered nanoscale semiconductor dots by ion sputtering. *Science* 285, 1551-1553.
- FEI company (2004). Quanta 3D FIB operation manual.
- Flamm, D., Frost, F. and Hirsch, D. (2001). Evolution of surface topography of fused silica by ion beam sputtering. *Applied Surface Science* 179, 95-101.
- Frey, L., Lehrer, C. and Ryssel, H. (2003). Nanoscale effects in focused ion beam processing. *Applied Physics A* 76, 1017-1023.
- Gago, R., Vazquez, L., Cuerno, R., Varela, M., Ballesteros, C. and Albella, J. M. (2001). Production of ordered silicon nanocrystals by low-energy ion sputtering. *Applied Physics Letters* 78, 3316-3318.
- Gago, R., Vazquez, L., Cuerno, R., Varela, M., Ballesteros, C. and Albella, J. M. (2002). Nanopatterning of silicon surfaces by low-energy ion-beam sputtering: dependence on the angle of ion incidence. *Nanotechnology* 13, 304-308.
- Gamo, K. and Namba, S. (1990). Micromachining using focused ion beams. *Microelectronic Engineering* 11, 403-408.
- Ghoniem, N. M., Walgraef, D. and Zinkle, S. J. (2002). Theory and experiment of nanostructure self-organization in irradiated materials. *Journal of Computer-Aided Materials Design* 8, 1-38.

References

- Giannuzzi, L. A. and Stevie, F. A. (1999). A review of focused ion beam milling techniques for TEM specimen preparation. *Micron* 30, 197-204.
- Giannuzzi, L. A. and Stevie, F. A. (2005). Introduction to Focused Ion Beams. New York, Springer.
- Gierak, J., Bourhis, E., Merat Combes, M. N., Chriqui, Y., Sagnes, I., Mailly, D., Hawkes, P., Jede, R., Bruchhaus, L. and Bardotti, L. (2005). Exploration of the ultimate patterning potential achievable with focused ion beams. *Microelectronic Engineering* 78-79, 266-278.
- Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Lyman, C. E., Lifshin, E., Sawyer, L. and Michael, J. R. (2003). Scanning Electron Microscopy and X-Ray Microanalysis. New York, Kluwer Academic/Plenum Publishers.
- Greene, J. P., Nemanich, J., Thomas, G. E. and Schiel, S. L. (1997). Noble gas sputtering calculations using TRIM. *Nuclear Instruments and Methods in Physics Research Section A* 397, 91-98.
- Grove, W. R. (1853). *Philosophical Magazine* 2, 203.
- Habenicht, S., Bolse, W., Feldermann, H., Geyer, U., Hofsass, H., Lieb, K. P. and Roccaforte, F. (2000). Ripple topography of ion-beam-eroded graphite: A key to ion-beam-induced damage tracks. *Europhysics Letters* 50, 209.
- Haff, P. K. (1977). A model for surface layer composition changes in sputtered alloys and compounds. *Applied Physics Letters* 31, 259-260.
- Her, T.-H., Finlay, R. J., Wu, C. and Mazur, E. (2000). Femtosecond laser-induced formation of spikes on silicon. *Applied Physics A* 70, 383 - 385.
- Herring, C. (1950). Effect of change of scale on sintering phenomena. *Journal of Applied Physics* 21, 301-303.

References

- Ho, P. S., Lewis, J. E. and Chu, W. K. (1979). Preferred sputtering on binary alloy surfaces of the Al-Pd-Si system. *Surface Science* 85, 19-28.
- Huang, M. H., Mao, S., Feick, H., Yan, H., Wu, Y., Kind, H., Weber, E., Russo, R. and Yang, P. (2001). Room-temperature ultraviolet nanowire nanolasers. *Science* 292, 1897-1899.
- Jach, T., Gormley, J., Thurgate, S. (1999). Grazing incidence X-ray photoemission spectroscopy of SiO₂ on Si. *Spectrochimica Acta Part B* 54, 1539-1544.
- Jones, K. S., Santana, C. J. (1991). Amorphization of elemental and compound semiconductors upon ion-implantation. *Journal of Materials Research* 6, 1048-1054.
- Kahng, B., Jeong, H. and Barabási, A.-L. (2001). Quantum dot and hole formation in sputter erosion. *Applied Physics Letters* 78, 805-807.
- Kahng, B. and Kim, J. (2004). Nanoscale pattern formations on surface induced by ion sputtering. *Current Applied Physics* 4, 115-120.
- Kanaya, K. and Okayama, S. (1972). Penetration and energy-loss theory of electrons in solid targets. *Journal of Physics D: Applied Physics* 5, 43-58.
- Karmakar, P. and Ghose, D. (2004). Ion beam sputtering induced ripple formation in thin metal films. *Surface Science* 554, L101-L106.
- Kiely, J. D. and Bonnell, D. A. (1997). Quantification of topographic structure by scanning probe microscopy. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 15, 1483-1493.
- Kim, J., Kahng, B. and Barabási, A.-L. (2002). Nanoscale wire formation on sputter-eroded surfaces. *Applied Physics Letters* 81, 3654-3656.
- Krohn, V. E. and Ringo, G. R. (1975). Ion source of high brightness using liquid metal. *Applied Physics Letters* 27, 479-481.

References

- Latif, A. (2000). Nanofabrication using focused ion beam. PhD thesis, University of Cambridge.
- Lee, J.-S., Park, K., Kang, M.-I., Park, I.-W., Kim, S.-W., Cho, W. K., Han, H. S. and Kim, S. (2003). ZnO nanomaterials synthesized from thermal evaporation of ball-milled ZnO powders. *Journal of Crystal Growth* 254, 423-431.
- Li, J., Stein, D., McMullan, C., Branton, D., Aziz, M. J. and Golovchenko, J. A. (2001). Ion-beam sculpting at nanometre length scales. *Nature* 412, 166-169.
- Li, Y., Meng, G. W., Zhang, L. D. and Phillipp, F. (2000). Ordered semiconductor ZnO nanowire arrays and their photoluminescence properties. *Applied Physics Letters* 76, 2011-2013.
- Liu, X., Du, D. and Mourou, G. (1997). Laser ablation and micromachining with ultrashort laser pulses. *IEEE Journal of Quantum Electronics*, 33, 1706-1716.
- Lugstein, A., Basnar, B. and Bertagnolli, E. (2004a). Metallic nano dots realized by a subtractive self organization process. *Superlattices and Microstructures* 36, 107-111.
- Lugstein, A., Basnar, B. and Bertagnolli, E. (2004b). Size and site controlled Ga nanodots on GaAs seeded by focused ion beams. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 22, 888-892.
- Lugstein, A., Basnar, B. and Bertagnolli, E. (2004c). Study of the chemical and morphological evolution of the GaAs surface after high fluence focused ion beam exposure. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 217, 402-408.
- Lugstein, A., Basnar, B., Hobler, G. and Bertagnolli, E. (2002). Current density profile extraction of focused ion beams based on atomic force microscopy contour profiling of nanodots. *Journal of Applied Physics* 92, 4037-4042.
- MacLaren, S. W., Baker, J. E., Finnegan, N. L. and Loxton, C. M. (1992). Surface roughness development during sputtering of GaAs and InP: Evidence for the role of

surface diffusion in ripple formation and sputter cone development. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 10, 468-476.

Makeev, M. A. and Barabási, A.-L. (1997). Ion-induced effective surface diffusion in ion sputtering. *Applied Physics Letters* 71, 2800-2802.

Makeev, M. A. and Barabási, A.-L. (1998a). Effect of surface roughness on the secondary ion yield in ion sputtering. *Applied Physics Letters* 73, 1445-1447.

Makeev, M. A. and Barabási, A.-L. (1998b). Secondary ion yield changes on rippled interfaces. *Applied Physics Letters* 72, 906-908.

Makeev, M. A., Cuerno, R. and Barabási, A.-L. (2002). Morphology of ion-sputtered surfaces. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 197, 185-227.

Malherbe, J. B. (2003). Bombardment-induced ripple topography on GaAs and InP. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 212, 258-263.

Malherbe, J. B. and Barnard, W. O. (1991). Preferential sputtering of InP: an AES investigation. *Surface Science* 255, 309-320.

Malherbe, J. B., van der Berg, N. G., Claudel, F., Osman, S. O. S., Odendaal, R. Q., Krok, F. and Szymonski, M. (2005). Fluence dependence of the surface roughness of InP after bombardment. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 230, 533-538.

Melngailis, J. (1987). Critical review: focused ion beam technology and applications. *Journal of Vacuum Science & Technology B* 5, 469-495.

Michely, T. and Comsa, G. (1993). The scanning tunneling microscope as a means for the investigation of ion bombardment effects on metal surfaces. *Nuclear Instruments*

and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 82, 207-219.

Micrion (1997). Micrion 9000/9100/9500 focused ion beam systems operation manual. Micrion Corporation.

Mongeot, F. B. d., Costantini, G., Boragno, C. and Valbusa, U. (2000). Ripple rotation in multilayer homoepitaxy. *Physical Review Letters* 84, 2445-2448.

Mullins, W. W. (1959). Flattening of a nearly plane solid surface due to capillarity. *Journal of Applied Physics* 30, 77-83.

Murty, M. V. R., Curcic, T., Judy, A., Cooper, B. H., Woll, A. R., Brock, J. D., Kycia, S. and Headrick, R. L. (1998). X-Ray Scattering Study of the Surface Morphology of Au(111) during Ar⁺ Ion Irradiation. *Physical Review Letters* 80, 4713-4716.

Musil, C. R., Melngailis, J., Etchin, S. and Haynes, T. E. (1996). Dose-rate effects in GaAs investigated by discrete pulsed implantation using a focused ion beam. *Journal of Applied Physics* 80, 3727-3733.

Naumann, J., Osing, J., Quinn, A. J. and Shvets, I. V. (1997). Morphology of sputtering damage on Cu(111) studied by scanning tunneling microscopy. *Surface Science* 388, 212-219.

Navez, M., Sella, C. and Chaperot, D. (1962). Investigation of the attack on glass by ion bombardment. *Comptes Rendus* 254, 240-242.

Nord, J., Nordlund, K., Keinonen, J. (2002). Amorphization mechanism and defect structures in ion-beam-amorphized Si, Ge, and GaAs. *Physical Review B* 65, 165329.

Onderdelinden, D. (1966). The influence of channeling on Cu single-crystal sputtering. *Applied Physics Letter* 8, 189-190.

References

- Ondrejcek, M., Swiech, W., Rajayppan, M. and Flynn, C. P. (2003). Ripples formed in the sputter erosion of Pd(111). *Journal of Physics: Condensed Matter* 15, L735-L742.
- Orloff, J. (1997). Handbook of Charged Particle Optics. Boca Raton, CRC Press.
- Orloff, J., Swanson, L. and Utlaut, M. (2002). High Resolution Focused Ion Beams: Fib and Its Applications: The Physics of Liquid Metal Ion Sources and Ion Optics and Their Application to Focused Ion Beam Technology. Plenum Pub Corp.
- Orloff, J., Utlaut, M. and Swanson, L. (2003). High resolution focused ion beams: FIB and its applications. New York, Kluwer Academic/Plenum Publishers.
- Overwijk, M. H. F., Heuvel, F. C. v. d. and Bulle-Lieuwma, C. W. T. (1993). Novel scheme for the preparation of transmission electron microscopy specimens with a focused ion beam. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 11, 2021-2024.
- Pan, J. S., Wee, A. T. S., Huan, C. H. A., Tan, H. S. and Tan, K. L. (1997). ARXPS analysis of surface compositional change in Ar^+ ion bombarded GaAs (100). *Journal of Physics D: Applied Physics* 30, 2514-2519.
- Pan, Z. W., Dai, Z. R. and Wang, Z. L. (2001). Nanobelts of Semiconducting Oxides. *Science* 291, 1947-1949.
- Park, S., Kahng, B., Jeong, H. and Barabási, A.-L. (1999). Dynamics of Ripple Formation in Sputter Erosion: Nonlinear Phenomena. *Physical Review Letters* 83, 3486-3489.
- Pellerin, J. G., Griffis, D. P. and Russell, P. E. (1990). Focused ion beam machining of Si, GaAs, and InP. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 8, 1945-1950.

References

- Pellerin, J. G., Shedd, G. M., Griffis, D. P. and Russell, P. E. (1989). Characterization of focused ion beam micromachined features. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 7, 1810-1812.
- Politi, P. and Villain, J. (1996). Ehrlich-Schwoebel instability in molecular-beam epitaxy: A minimal model. *Physical Review B* 54, 5114-5129.
- Prenitzer, B. I. (1999). Investigation of variables affecting focused ion beam milling as applied to specimen preparation for electron microscopy: a correlation between Monte Carlo based simulation and empirical observation. PhD thesis, University of Central Florida.
- Prewett, P. D. and Mair, G. L. R. (1991). Focused ion beams from liquid metal ion source. Research Studies Press.
- Qian, H. X., Zhou, W., Fu, Y. Q., Ngoi, B. K. A. and Lim, G. C. (2005). Crystallographically-dependent ripple formation on Sn surface irradiated with focused ion beam. *Applied Surface Science* 240, 140-145.
- Reyntjens, S. and Puers, R. (2001). A review of focused ion beam applications in microsystem technology. *Journal of Micromechanics and Microengineering* 11, 287-300.
- Ritter, M., Stindtman, M., Farle, M. and Baberschke, K. (1996). Nanostructuring of the Cu(001) surface by ion bombardment: a STM study. *Surface Science*. 348, 243-252.
- Rol, P. K., Fluit, J. M. and Kistemaker, J. (1960). Theoretical aspects of cathode sputtering in the energy range of 5-25 keV. *Physica* 26, 1009-1011.
- Rost, M. and Krug, J. (1995). Anisotropic Kuramoto-Sivashinsky equation for surface growth and erosion. *Physical Review Letters* 75, 3894-3897.
- Rusponi, S., Boragno, C. and Valbusa, U. (1997). Ripple structure on Ag(110) surface induce by ion sputtering. *Physical Review Letters* 78, 2795-2798.

References

- Rusponi, S., Costantini, G., Boragno, C. and Valbusa, U. (1998a). Ripple wave vector rotation in anisotropic crystal sputtering. *Physical Review Letters* 81, 2735-2738.
- Rusponi, S., Costantini, G., Boragno, C. and Valbusa, U. (1998b). Scaling laws of the ripple morphology on Cu(110). *Physical Review Letters* 81, 4184-4187.
- Rusponi, S., Costantini, G., Buatier de Mongeot, F., Boragno, C. and Valbusa, U. (1999). Patterning a surface on the nanometric scale by ion sputtering. *Applied Physics Letters* 75, 3318-3320.
- Saitoh, H., Satoh, M., Tanaka, N., Ueda, Y. and Ohshio, S. (1999). Homogeneous growth of zinc oxide whiskers. *Japanese Journal of Applied Physics, Part 1 (Regular Papers, Short Notes & Review Papers)* 38, 6873-6877.
- Schmuki, P., Erickson, L. E., Champion, G., Mason, B. F., Fraser, J. and Moessner, C. (1997). Surface topology of GaAs(100) after focused ion beam implantation of Si^{++} . *Applied Physics Letters* 70, 1305-1307.
- Schwoebel, R. L. and Shipsey, E. J. (1968). *Journal of Applied Physics* 40, 614.
- Sekiba, D., Moroni, R., Gonella, G., Mongeot, F. B. d., Boragno, C., Mattera, L. and Valbusa, U. (2004). Uniaxial magnetic anisotropy tuned by nanoscale ripple formation: Ion-sculpting of Co/Cu(001) thin films. *Applied Physics Letters* 84, 762-764.
- Seliger, R. L., Ward, J. W., Wang, V. and Kubena, R. L. (1979). A high-intensity scanning ion probe with submicrometer spot size. *Applied Physics Letters* 34, 310-312.
- Shin, K., Leach, K. A., Goldbach, J. T., Kim, D. H., Jho, J. Y., Tuominen, M., Hawker, C. J. and Russell, T. P. (2002). A Simple Route to Metal Nanodots and Nanoporous Metal Films. *Nano Letters* 2, 933-936.
- Shirk, M. D. and Molian, P. A. (1998). A review of ultrashort pulsed laser ablation of materials. *Journal of Laser Applications* 10, 18-28.

References

- Sigmund, P. (1969). Theory of Sputtering. I. Sputtering Yield of Amorphous and Polycrystalline Targets. *Physical Review* 184, 383-416.
- Sigmund, P. (1973). A mechanism of surface micro-roughening by ion bombardment. *Journal of Materials Science* 8, 1545-1553.
- Sigmund, P. (1980). Sputtering of single and multiple component materials. *Journal of Vacuum Science and Technology* 17, 396-399.
- Singer, I. L., Murday, J. S. and Cooper, L. R. (1981). Surface composition changes in GaAs due to low-energy ion bombardment. *Surface Science* 108, 7-24.
- Smentkowski, V. S. (2000). Trends in sputtering. *Progress in Surface Science* 64, 1-58.
- Southern, A. L., Willis, W. R. and Robinson, M. T. (1963). Sputtering Experiments with 1- to 5-keV Ar⁺ Ions. *Journal of Applied Physics* 34, 153-163.
- Spanos, L. and Irene, E. A. (1994). Investigation of roughened silicon surfaces using fractal analysis. I. Two-dimensional variation method. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 12, 2646-2652.
- Steckl, A. J., Chen, P., Jackson, H. E., Choo, A. G., Cao, X., Boyd, J. T. and Kumar, M. (1995). Review of focused ion beam implantation mixing for the fabrication of GaAs-based optoelectronic devices. *Journal of Vacuum and Science Technology B* 13, 2570-2575.
- Steckl, A. J. and Chyr, I. (1999). Focused ion beam micromilling of GaN and related substrate materials (sapphire, Sic, and Si). *Journal of Vacuum and Science Technology B* 17, 362-365.
- Stepanova, M., Dew, S. K. and Soshnikov, I. P. (2002). Sputtering from ion-beam-roughened Cu surfaces. *Physical Review B* 66, 125407-1-8.

References

- Stroschio, J. A., Pierce, D. T., Stiles, M. D., Zangwill, A. and Sander, L. M. (1995). Coarsening of Unstable Surface Features during Fe(001) Homoepitaxy. *Physical Review Letters* 75, 4246-4249.
- Sugiyama, M. and Sigesato, G. (2004). A review of focused ion beam technology and its applications in transmission electron microscopy. *Journal of Electron Microscopy* 53, 527-536.
- Sundaram, S. K. and Mazur, E. (2002). Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses. *Nature Materials* 1, 217-224.
- Teichert, C., Hohage, M., Michely, T. and Comsa, G. (1994). Nuclei of the Pt(111) network reconstruction created by single ion impacts. *Physical Review letters* 72, 1682-1685.
- Thurmer, K., Koch, R., Weber, M. and Rieder, K. H. (1995). Dynamic evolution of pyramid structures during growth of epitaxial Fe (001) films. *Physical Review letters* 75, 1767-1770.
- Townsend, P. D., Kelly, J. C. and Hartley, N. E. W. (1976). Ion implantation, sputtering and their applications. London, Academic Press Inc.
- Tseng, A. A. (2004). Recent developments in micromilling using focused ion beam technology. *Journal of Micromechanics and Microengineering* 14, R15-R34.
- Vajo, J. J., Doty, R. E. and Cirlin, E.-H. (1996). Influence of O_2^+ energy, flux, and fluence on the formation and growth of sputtering-induced ripple topography on silicon. *Journal of Vacuum and Science Technology A* 14, 2709-2720.
- Valbusa, U., Boragno, C. and Buatier de Mongeot, F. (2003). Nanostructuring by ion beam. *Materials Science and Engineering: C* 23, 201-209.
- Valbusa, U., Boragno, C. and Mongeot, F. B. d. (2002). Nanostructuring surfaces by ion sputtering. *Journal of Physics: Condensed Matter* 14, 8153-8175.

References

- Verkleij, D. (1998). The use of the focused ion beam in failure analysis. *Microelectronic Reliability* 38, 869-876.
- Villain, J. (1991). Continuum models of crystal growth from atomic beams with and without desorption. *Journal of Physics (France)* I 1, 19-42.
- Walker, J. F., Moore, D. F. and Whitney, J. T. (1996). Focused ion beam processing for microscale fabrication. *Microelectronic Engineering* 30, 517-522.
- Wang, L. M. (1998). Applications of advanced electron microscopy techniques to the studies of radiation effects in ceramic materials. *Nuclear Instruments and Methods in Physics Research B* 141, 312.
- Wang, Z. L. (2004). Nanostructures of zinc oxide. *Materials Today* 7, 26-33.
- Wehner, G. K. (1956). Controlled sputtering of metals by low-energy Hg ions. *Physical Review* 102, 690-704.
- Wehner, G. K. (1960). Forces on ion-bombarded electrodes in a low-pressure plasma. *Journal of Applied Physics* 31, 1392-1397.
- Xu, X., Ratta, A. D. D., Sosonkina, J. and Melngailis, J. (1992). Focused ion beam induced deposition and ion milling as a function of angle of ion incidence. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 10, 2675-2680.
- Yamaguchi, H., Shimase, A., Haraichi, S. and Miyauchi, T. (1985). Characteristics of silicon removal by fine focused gallium ion beam. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 3, 71-74.
- Young, R. J., Cleaver, J. R. A. and Ahmed, H. (1993). Characteristics of gas-assisted focused ion beam etching. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 11, 234-241.

References

Yu, W., Sullivan, J. L., Saied, S. O. and Jones, G. A. C. (1998). Ion bombardment induced compositional changes in GaP and InP surfaces. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 135, 250-255.

Yurasova, V. and Eltekov, V. (1982). Models of single crystal sputtering. *Vacuum* 32, 399-424.

Zhou, W., Cuenat, A. and Aziz, M. J. (2003). Formation of self-organized nanostructures on Ge during focused ion beam sputtering. *Microscopy of Semiconducting Materials 2003: Proceedings of the 13th International Conference on Microscopy of Semiconducting Materials*, Cambridge University, Institute of Physics and IOP publishing Limited, 625-628.

Ziegler, J. F., SRIM 2003, www.srim.org

Ziegler, J. F., Biersack, J. P. and Littmark, U. (1985). The stopping and range of ions in solids. New York, Pergamon Press.

Zuo, J.-K. and Wendelken, J. F. (1997). Evolution of mound morphology in reversible homoepitaxy on Cu(100). *Physical Review Letters* 78, 2791-2794.

Appendix A

Morphological and Chemical Evolution on InP(100) Surface Irradiated with Femtosecond Laser

Abstract

Single crystalline InP was ablated in air with p-polarized Ti:sapphire femtosecond laser at a fixed laser fluence of 82 mJ/cm^2 . Ripples parallel to the laser polarization direction were found by scanning electron microscopy and atomic force microscopy to form for laser pulses ranging from 50 to 1000, whereas flower-like structures appeared for laser pulses of 10^4 and above. Analysis by x-ray photoelectron spectroscopy showed formation of indium and phosphorus oxides on the irradiated surface and the amounts of oxides increased with increasing number of laser pulses. The oxide formation is attributed to chemical reaction between the ultrafast laser ablation plume and oxygen in air, and formation of the flower-like structures is shown to be related to deposition of the oxides on the irradiated surface.

Pacs Codes: 79.60.-i; 82.53.-k; 81.65.Mq; 79.20.Ds

Keywords: Indium phosphide; X-ray photoelectron spectroscopy; Oxidation; Ripples

1. Introduction

InP is one of the most important III-V semiconductors used for electronic [1] and optoelectronic [2] applications. Femtosecond laser provides a high precision method for micromachining of semiconductors with minimal damage [3,4]. Study of InP surface irradiated with femtosecond laser is of much interest to both academic and industrial worlds. We aimed to study chemical and morphological changes on InP surface irradiated in air with increasing number of femtosecond laser pulses.

Dubreuil and Gibert [5] studied laser processing of InP as early as in 1994, but they used a nanosecond laser in ultra-high vacuum. Borowiec and Haugen [6] studied subwavelength ripple formation on surfaces of InP and other semiconductor compounds irradiated with femtosecond laser but the experiment was also carried out in vacuum. Borowiec et al. [7] carried out detailed TEM-based studies of single-pulse femtosecond laser irradiation of InP for various fluences and provided important information on both subtle and extensive surface modifications due to the laser irradiation. However, they did not study the chemical or morphological changes with increasing number of pulses since the study was limited to single pulse irradiation in vacuum.

Bonse et al. [8,9] carried out systematic researches on femtosecond laser ablation of InP in air. They established the dependence of the ablation threshold fluence on the number of pulses applied to the same spot [8], obtained experimental results to show the formation of oxides by means of AES (Auger Electron Spectroscopy) [8], and characterized the surface morphological evolution with increasing number of pulses [8,9] using SEM (Scanning Electron Microscopy). We carried out XPS (X-ray Photoelectron Spectroscopy) study and provided further evidence to show the formation of indium and phosphorus oxides due to femtosecond laser irradiation in air. Furthermore, we studied the surface morphological evolution from a small number of

pulses to 10^5 using various surface characterization tools including SEM, AFM (Atomic Force Microscopy), and a 3D surface profiler. Ripples with “unusual” orientation were observed for small number of pulses, and flower-like structures were observed on surfaces irradiated with more than 10^3 pulses. To the best of our knowledge, this is the first report on the flower-like structures on the femtosecond laser irradiated surface.

2. Experimental

An un-doped InP(100) wafer was irradiated with p-polarized femtosecond laser (Clark-MXR CPA-2010) in air. The laser emits 150 fs pulses of linearly polarized light at a central wavelength of 775 nm and with repetition rate of 1 kHz. Beam entrance diameter is 3.5 mm. The wafer was placed at a position of 4 mm away from the focal plane of the focusing lens (focal length $f = 50$ mm). The laser beam was directed perpendicularly onto the sample surface. The laser power was fixed at 55 mW. The nominal laser beam spot diameter at the off-focal plane was about 293 μm . The single pulse energy was 55 μJ and laser fluence was calculated to be 82 mJ/cm^2 . The number of laser pulses was varied from 50 to 10^5 to study its effect on morphological and chemical change.

Surface chemistry for areas irradiated with laser was studied using XPS (Kratos-Axis spectrometer) with monochromatic Al $K\alpha$ (1486.71 eV). High resolution scans were collected with pass energy of 40 eV and step of 0.1 eV. The analyzing chamber pressure fluctuated between 10^{-8} and 10^{-9} Torr. The spectra were calibrated using C 1s peak position at 284.6 eV.

Morphology of the irradiated surface was examined using SEM (CamScan S360) and AFM (Nanoscope IIIa). For the very rough surfaces which cannot be characterized with AFM, 3D measurements were carried out using a Taylor Hobson Precision Talysurf profiler operated at non-contact mode.

3. Results and Discussion

After the InP surface was irradiated with 50 consecutive laser pulses, ripples were observed. Figs. 1(a) and 1(b) show SEM and AFM images of the ripples respectively. The depth of the ripples is about 120 nm as measured by AFM. Similar ripples were observed on surface irradiated with number of pulses ranging from 50 to 1000. The ripple period is not sensitive to the number of pulses and it is roughly equal to three quarters of laser wavelength (775nm). Orientation of the ripples was always found to be parallel to the laser polarization direction.

Fig.1. SEM micrograph (a) and AFM image (b) showing formation of ripples parallel to laser polarization direction at a laser fluence of 82 mJ/cm^2 and 50 pulses.

Laser-induced ripple formation is a common phenomenon. Many researchers report ripples with period close to the incident laser wavelength and aligned perpendicular to the laser polarization direction [10,11]. It is generally accepted that the ripple formation is due to the optical interference between the incident wave and a surface scattered electromagnetic wave [12-14]. Subwavelength ripple formation has also been found on laser irradiated surfaces of many materials, including diamond film [15], TiN [16], InP [6,9], GaAs and GaP [6].

The ripple orientation observed in the present study is in contrast with that reported by many others [6-11]. In particular, Borowiec et al. [6] and Bonse et al. [8,9] reported ripples perpendicular to laser polarization direction on InP surface. However, it is noted that Borowiec et al. [6] used femtosecond lasers with much longer wavelengths (1300 nm and 2100 nm instead of 775 nm), and even in that case some surface features orientated parallel to laser polarization direction can be seen to be present on the irradiated surface, as shown in Fig. 1(b) in Ref. [6] (though the predominant surface features are those ripples perpendicular to laser polarization direction). Although Bonse et al. [8,9] reported formation of ripples perpendicular to laser polarization direction, they also observed the morphological change from the ripples to so-called “grooves” when the number of laser pulses increased to 100 (see Fig. 4(d) in Ref. [8] and Fig. 6 in Ref. [9]). It should be especially noted that the periodic surface features described as “grooves” are in fact parallel to the laser polarization direction and thus resemble the ripples observed in the present study. In addition, Wu et al. [17] also observed, on surface of unpolished diamond film irradiated with p-polarized femtosecond laser, ripples parallel to the laser polarization as well as those perpendicular to the polarization.

For much higher number of pulses ranging from 10^4 to 10^5 , ripples disappeared and flower-like structures (which are so named due to their similarity in appearance to flowers) occurred on the irradiated surface. One typical area irradiated with 3×10^4 consecutive pulses is shown in Fig. 2. Light-colored patches were observed on the irradiated surface under the SEM (Fig. 2(a)) and observation of the patches at higher magnifications revealed flower-like surface structures (Fig. 2(b)). The spongy and dendritic appearance of the structures suggest they might be formed due to redeposition of ablated material or deposition of In and P oxides formed in the laser ablation plume in air. This assumption is supported by experimental results to be presented below.

Fig. 2. Observation of flower-like structures at laser fluence of 82 mJ/cm^2 and 3×10^4 pulses. (a) Overall SEM image. (b) Close-up of light-colored patches in (a) showing flower-like structures. (c) Image from 3D surface profiler indicating that the flower-like structures protrude above the original surface by more than 30 μm . (d) Optical micrograph of the irradiated area.

The surface irradiated with large number of pulses is too rough to be characterized with AFM, so the Talysurf surface profiler was used to study the surface topography. The flower-like structures were found to protrude above the original surface by more than 30 μm , as shown in Fig. 2(c). This observation lends further support to the assumption that the flower-like structures formed as a result of material redeposition during laser ablation.

Fig. 2(d) is an optical micrograph of the same laser irradiated area as shown in Figs. 2(a) and 2(c). The surface is very rough and therefore expected to deflect light and give dark optical image; however, it is surprising that the very rough surface can be imaged quite clearly using the optical microscope, indicating that the flower-like structures might have different optical properties.

XPS was used to analyze the surface chemistry of irradiated areas. High-resolution XPS scans of In 3d cores for as-received and Ar ion etched InP surface are shown in Fig. 3. The In 3d core is spin-orbit split into $3d_{5/2}$ and $3d_{3/2}$ peaks. For the as-received surface, the In $3d_{5/2}$ region has two peaks, one at 443.7 eV due to bonding between In and P and the other one at 444.8 eV due to surface contamination (the peak at 444.8 eV disappeared after the contamination was removed after Ar ion etching for 10 min).

Fig. 4 shows the In 3d spectra for InP surface irradiated with varying number of pulses. The spectra of the surface irradiated with 10^2 and 10^3 pulses still exhibit features of the substrate InP (In $3d_{5/2}$ at 443.7 eV and In $3d_{3/2}$ at 451.2 eV), as shown in Figs. 4(a) and 4(b). However, when the number of pulses increased to 10^4 and 10^5 , In-P bonding could no longer be detected and new peak positions appeared with $3d_{5/2}$ at 442.9 eV and $3d_{3/2}$ at 450.4 eV. The new peaks might be due to metallic indium. Indium oxide was found to form with $3d_{5/2}$ at 445.1 eV and $3d_{3/2}$ at 452.6 eV for all the laser irradiated surfaces and the amount of the oxide was found to increase with increasing number of pulses.

Fig. 3. XPS spectra of In 3d core for as-received surface and Ar ion sputtered surface.

Fig. 4. XPS spectra showing In 3d cores for surfaces irradiated at a laser fluence of 82 mJ/cm² with a different number of laser pulses. (a) 10^2 , (b) 10^3 , (c) 10^4 , and (d) 10^5 .

Fig. 5. XPS spectra showing P 2p cores for InP surfaces irradiated at a laser fluence of 82 mJ/cm^2 with varying number of laser pulses (a) 10^2 , (b) 10^3 , (c) 10^4 , and (d) 10^5 .

Fig. 5 shows the P 2p spectra for InP surface irradiated with varying number of laser pulses. Similarly, phosphorus oxide formed for all the laser pulses studied. As can be seen from Fig. 5, P 2p at 133.3 eV is due to oxidized P species, and P 2p at 128.1 eV is due to InP. The amount of phosphorus oxides was also found to increase with increasing laser pulses.

The XPS study, together with the AES study by Bonse et al. [8], provides strong evidence to show the formation of increasing amounts of indium and phosphorus oxides during femtosecond laser irradiation of InP in air. Chemical reactions to form the oxides cannot possibly complete in the ultrashort laser pulse duration of 150 fs (or 130 fs in the study by Bonse et al. [8]), so we attribute their formation to oxidation between oxygen in air and ablation plume induced by the ultrahigh intensity laser. The laser fluence used (82 mJ/cm^2) is far smaller than the threshold for plasma formation (1

J/cm²) as reported by Cavalleri et al. [18]; therefore, the ablation plume is likely to be composed of mono-atomic In and P and their molecular clusters.

Damage threshold is reported to be 160 mJ/cm² for single pulse ablation on InP using 130 fs laser at a wavelength of 800 nm [6,8]. In this study, the single pulse fluence used (82 mJ/cm²) is much lower, but the number of pulses used is larger. The specific processing parameters might account for the different observations on the surface of InP.

Femtosecond laser-induced structures other than the flower-like ones have been observed by others [19,20]. Her et al. [19] reported the formation of sharp conical spikes by femtosecond laser irradiation of silicon in the presence of SF₆. Further research by Sheehy et al. [20] shows that the presence of sulfur in the background gases is important in creating surface structures in sharp conical shape, suggesting that ambient gases play an essential role in determining surface morphology during femtosecond laser and material interaction.

It is hoped that the present study would stimulate further researches on the formation mechanisms of periodic surface features parallel to the laser polarization direction and innovative applications of the flower-like structures. It would also be interesting to study how ambient gases would affect surface pattern formation on InP.

4. Conclusion

The XPS study shows formation of In and P oxides on InP surface irradiated with femtosecond laser due to chemical reaction between the laser ablation plume and oxygen in air. Subwavelength ripples parallel to the laser polarization direction were found to form at low number of pulses. Flower-like spongy structures protruding above the original surface were observed on surface irradiated with much larger number of pulses as the result of deposition of the oxides. The surface oxidation may pose an engineering problem for high precision femtosecond laser micromachining of InP in air.

References

- [1] A. Mesquida Küsters, K. Heime, Solid-State Electron. 41 (1997) 1159.
- [2] S. Chandrasekhar, Solid-State Electron. 41 (1997) 1413.
- [3] J. Krüger, W. Kautek, Laser Phys. 9 (1999) 30.
- [4] P. P. Pronko, S. K. Dutta, J. Squier, J. V. Rudd, D. Du, G. Mourou, Opt. Commun. 114 (1995) 106.
- [5] B. Dubreuil, T. Gibert, J. Appl. Phys. 7545 (1994) 76.
- [6] A. Borowiec, H. K. Haugen, Appl. Phys. Lett. 82 (2003) 4462.
- [7] A. Borowiec, M. Mackenzie, G. C. Weatherly, H. K. Haugen, Appl. Phys. A 77 (2003) 411.
- [8] J. Bonse, J. M. Wrobel, J. Krüger, W. Kautek, Appl. Phys. A 72 (2001) 89.
- [9] J. Bonse, M. Munz, H. Sturm, J. Appl. Phys. 97 (2005) 013538.
- [10] N. R. Isenor, Appl. Phys. Lett. 31 (1977) 148.
- [11] G. Dumitru, V. Romano, H. Weber, M. Sentis, and W. Marine, Appl. Phys. A 74 (2002) 729.
- [12] D. C. Emmony, R. P. Howson, L. J. Willis, Appl. Phys. Lett. 23 (1973) 598.
- [13] G. S. Zhou, P. M. Fauchet, A. E. Siegman, Phys. Rev. B 26 (1982) 5366.
- [14] J. E. Sipe, J. F. Young, J. S. Preston, H. M. van Driel, Phys. Rev. B 27 (1983) 1141.
- [15] A. M. Ozkan, A. P. Malshe, T. A. Railkar, W. D. Brown, M. D. Shirk, R. A. Molian, Appl. Phys. Lett. 75 (1999) 3716.

- [16] N. Yasumaru, K. Miyazaki, J. Kiuchi, Appl. Phys. A 76 (2003) 983.
- [17] Q. H. Wu, Y. R. Ma, R. C. Fang, Y. Liao, Q. X. Yu, X. L. Chen and K. Wang, Appl. Phys. Lett. 82 (2003) 1703.
- [18] A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, M. Schreiner and D. von der Linde, J. Appl. Phys. 85 (1999) 3301.
- [19] T.-H. Her, R. J. Finlay, C. Wu and E. Mazur, Appl. Phys. A 70 (2000) 383.
- [20] M. A. Sheehy, L. Winston, J. E. Carey, C. M. Friend and E. Mazur, Chem. Mater. 17 (2005) 3582.