Surface Engineering Nanostructures

Low energy Ion bombardment nanostructuring Process

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Surface Engineering Nanostructures

**Top Down:** “Imposing” a pattern on the Substrate

- Photo-lithography: Expensive, 100nm
- Scanning Beam Lithography: Low deposition rate, 10 nm
- Scanning Probe Lithography: Low deposition rate, 1 nm

**Bottom Up:** Guiding the assembly of atoms or molecules

- Resolution: 1nm
- One step process
- Large Areas

**Ion Bombarding**

Top–Down and Bottom-Up hybrid

1) Sculpted Substrate By Ion Beam Bombarding
2) Ni Self–organized Structures Obtained on the sculpted substrate
**Bottom Up Fabrication: Mesoporous Patterned Silica (Sol Gel Technique)**

Silica Based Thin Film: cubic symmetry (polycondensation + evaporation + self-organization)

- 7 nm cavities sizes separated by ~1.8 nm walls

CVD Carbon Nanotubes Growth catalyzed by Ni

Surface Process: a brief introduction

- Atoms arrive from the vapor phase

- **Self-Organizing**: Mean Way between kinetic and thermodynamic phenomenon

- **Surface diffusion on a flat surface** (terrace): primary mechanism (**activated process**)

- Mean displacement *adatom* $\lambda$: distance before remains immobilized or detaching to the vapor

$$\lambda = \lambda_0 \exp \left[ \frac{(\varepsilon_s - u_s)}{2kT} \right]$$

$\varepsilon_s$: evaporation energies
$u_s$: activation energy

- **D/F>>1** Process Governed by Thermodynamic (Near Equilibrium)
- **D/F<<1** Process Governed by Kinetic

D= Diffusion Coefficient, F= Particles Flux

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Surfaces nano-structuration

- First Experiments by Ion Bombarding: Glass, Ionized air, 6 hs, 4 kV

Campinas Sky, SP, Brazil

Atacama Desert, Chile

Snow Ripples *Las Leñas*, Argentina
Sand(Snow) Dunes: At the hill or depression, Different Velocities

Clouds: ripples between the dry, cool air above and the moist, warm air below
Low energy Ion bombardment nano-structuring Process

Control Deposition Parameters

- Ion Species
- Ion Energy
- Impinging Angle
- Flux (Dose)
- Substrate Temperature
Experimental: Ion Beam

Noble gases Bombardment (NG\textsuperscript{+}): Ar\textsuperscript{+}, Kr, + Xe +

Energy
20 – 1200 eV
PO\textsubscript{2} < 10\textsuperscript{-8} mb

Current
~1mA/cm\textsuperscript{2}

 Ion gun (Kaufman)
SEM-FEG images: AISI 316L (Room T, Xe\(^+\), 1 keV)

- **Crystalline grains** evidenced
- **Patterns** within the crystalline grains

Cucatti, Alvarez., submitted, 2014
Nano-Structures on Semiconductors

Ar\(^+\), 2 KeV, perpendicular

GaSb, Gallium Antimonide

500nm

Hexagonal Symmetry

Facsko et al., Science 285, 1999, p1551

Xe\(^+\), Si (110), 1keV, 15°

Semiconductors Nano-structuration

Ion energy dependence

Substrate: Si, Ar+, Room Temperature

800 eV

1200 eV

2000 eV

1200 eV

800 eV

500 eV

Ziberi et al., J. Phys: Condens. Mat. 21 (2009)
Ion patterning: Bradley & Harper Model

Concave

Convex

Faster Erosion

TiN + Ni Particles Ion Beam Deposition

Nickel Particles
- 750°C
- 1.5 min deposition
- 5 min annealing

Ni Deposition + Annealing

Ni Atoms Flux

Annealing

- 750°C, 1.5 min, deposition
- 5 min annealing

Morales, Merlo, Droppa, Alvarez, J. of Phys: D, 2014 (014)
Atomic Force Microscopy

Fourier Transform

Conclusions

- Different possibilities generating regular nanostructures by ion bombarding

- Self-organized metallic nano-particles on sculpted patterned silicon

- Self-organization: Irregularities & defects still important

- Lack of general theoretical understanding about the general patterning and self-organization process
Put a three years old black goat in a locked room, without food; after the four day, feed the animal only with fern during two days. The following night, put the goat in a vat with holes in the button to collect the urine's goat. Store the urine of two or three nights and throw out the goat. Therefore, temper yours instruments in the collected urine.

Iron instruments are also very well tempered in the urine of a young red haired boy, giving more hardening that tempering simply in water.

Theophilus Presbyter (Roger of Helmarshhausen, Germany) (Monge Beneditino, 12th Century), *Scheme of Various arts*, translated to English from Hendrich, 1847.
Plasma-LIITS
Surfaces Plasma Processing
Daniel Wisnivesky
Fernando Alvarez

Instituto de Física “Gleb Wataghin”
UNICAMP, SP, Brazil

Supporting Agency: FAPESP
Gear Box Manufacturing

2004

Industrial Applications

Plasma Nitriding

Industry

Small Company
Equipment and Processes

Plasma-LIITS

Equipamentos e Processos
PRIMAR Y COMPANY GOALS

- Metallic Surfaces treatments by plasma: R & D
- Equipment for nitriding and coatings: R & D
- Alternative to Salt Bath and Ammonia
- Interaction with the industry
COMPANY EVOLUTION

PRODUCTS IN 2014

• Nitriding Equipments
• Pulsed Power Supply
• Hard Coating Equipments
• R&D: Processes and Equipments
• Industrial Consulting
• HiPIMS Equipments (High Power Impulse Magnetron Sputtering)
Nitriding Plant Fully Automatic

- Automatic Gas Console
- Vacuum Furnace
- CLP
- Pulsed Power Supply
- Heater Control
Roll-to-Roll Thin Film Deposition Solar Absorber Panels
Plasma Immersion (PI3) Nitriding System (25 keV) + Remote Auxiliary RF Plasma
High Speed Steel Cutting Tools
( M2, M35, M42)

Cold Work
( D2, D3, D6)

Molds for Plastic Injection+
Oxidation (P20, P50, H13)
Thanks for your attention
Thanks for your attention
Instability: Piling up along the terrace

$E_b \sim 0.45 \text{ eV}$
Self - Organization

Ehrlich-Shhwoebel (E-S) barrier
Steel100Cr6 (AISI 52100)

Stress

X-Ray diffraction

Implanted layer (~5-10 Å)

Modified region (~1 μ)

Bulk

Implantation Energy (eV)

Stress (MPa)

Initial compressive stress

x-ray penetration depth (~980nm)

Seeman-Bohlin
Replacement Collision Sequence (RCS)

Newton Cradle (Momentum Conservation)

Account for defects <10 nm depth*

Highly anharmonic localized excitations (such as a DB) which propagate distances well beyond the ion penetration depth can explain deeper defects†

Nitrided Case : SS 316

SS316; T=390 °C, 4 hs
Without pre-bombardment

SS316; T=390 °C, 4 hs
20 eV, Xe+ pre-bombarded
Grazing X-Ray Diffractograms

Pre-Bombarded and Nitrided SS316

\[ \gamma_N(111) \]

\[ \gamma(111) \]

\[ \gamma_N(200) \]

\[ \lambda = 1.5 \, 4056 \, \text{Å} \]

No Bombarded Nitrided 4 hs

Intensidade, u.a.

2\(\theta\), Grauss

X-Ray Penetration depth \(\sim 0.15-0.20 \, \mu\text{m}\)
Grazing X-Ray Diffractograms
Pre-Bombarded and Nitrided AISI 4140

$\lambda = 1.54056 \, \text{Å}$

Bragg-Brentano
$\theta=2^0$ grazing angle

$\varepsilon(002) + \gamma'(111)$

$\varepsilon(100)$

$\alpha(110)$

$\lambda = 1.54056 \, \text{Å}$

$\theta=2^0$ grazing angle

$\varepsilon(002) + \gamma'(111)$

$\varepsilon(100)$

$\alpha(110)$

$T = 400 \, ^0\text{C}, 30$

$\gamma'(200)$

X-Ray Penetration depth $\sim 0.15-0.20 \, \mu\text{m}$

3 KV, Xe$^+$
**Nitrogen Concentration**

Sputtered Neutral Mass Spectroscopy

- Only nitriding (0.5 hr) AISI 4140, 400 °C
- Xe⁺ pre-treatment (125 eV) + nitriding (0.5 hr)

**Diffusion Coefficient**

**Polycrystalline multiphase system ε, γ´, α**

From the Phase diagram Fe-N: C´s

**Adapted from P. Hansen, Phys. Metal., 2003**

<table>
<thead>
<tr>
<th>Diffusion coefficient</th>
<th>I=Without Pre-treatment</th>
<th>II=With Pre-treatment</th>
<th>Ratio II/I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_\varepsilon$ ($\mu m^2/s$)</td>
<td>$0.88 \times 10^{-4}$</td>
<td>$3.7 \times 10^{-4}$</td>
<td>4.6</td>
</tr>
<tr>
<td>$D_{\gamma'}$ ($\mu m^2/s$)</td>
<td>$3.4 \times 10^{-4}$</td>
<td>$6.9 \times 10^{-4}$</td>
<td>2</td>
</tr>
<tr>
<td>$D_\alpha$ ($\mu m^2/s$)</td>
<td>0.32</td>
<td>0.32</td>
<td>1</td>
</tr>
</tbody>
</table>

**Grain border, dislocations**

- Lower packing density
- Faster diffusion

“Irrigation channel”

Only nitriding (0.5 hr)  
Xe⁺ pre-treatment (125 eV) + nitriding (0.5 hr)
Conclusions

- Atomic Attrition: nanoscopic scale grain refining
- Implantation \textit{(knock-on)} Xe\(^+\), Kr\(^+\), Ar\(^+\): stress
- Thermal spike: relaxation
- Sequential Collision Effect
- Deeper changes due to other effects: e.g.: DB
- Increasing Nitrogen Retention at Surface
- Increasing effective diffusion coefficient
- Decreasing process time
- Improving Nitrogen Diffusion: thicker case

Thanks for your attention
Bragg-Brentano geometry

The Bragg-Brentano geometry is the most used among diffractometers. In the diffractometer the relationship between $\theta$ (the angle between the direction of the incident beam and the specimen surface) and $2\theta$ (the angle between the directions of incident beam and the diffracted beam) is maintained throughout the analysis. $r_s$ and $r_d$ are fixed and equal and define the diffractometer- or measuring circle in which the specimen is always at the centre. The geometry is called $\theta - 2\theta$ geometry if the tube is fixed and the rotation of the specimen and receiving slit are coupled in a ratio $\theta : 2\theta$. It is called $\theta - \theta$ geometry if the specimen is fixed and both the tube and receiving slit rotate at an equal angle $\theta$. During rotation of the components the radius of the focusing circle changes.

Seeman-Bohlin geometry

The Seeman-Bohlin diffractometer can have a fixed tube and specimen. The radius $r_d$ varies with $2\theta$ to maintain the focusing geometry. Alternatively the source and receiving slit rotate at an equal angle $\theta$ and both $r_s$ and $r_d$ vary to remain on the focusing circle. During rotation of the components the radius of the focusing circle remains the same.
ESTUDO DA NANOESTRUTURAÇÃO DE SUBSTRATOS CRISTALINOS ATRAVÉS DO BOMBARDEAMENTO COM FEIXE DE ÍONS A BAIXA ENERGIA

Mónica Morales Corredor
Orientador: Prof. Dr. Fernando Alvarez

Exame de Qualificação de Doutorado

Campinas, abril de 2014
Sumário

- Motivação
- Métodos
- Exemplos de Nano-estruturação de superfícies
- Modelo do Bombardeamento com feixe de Íons
- Experimento
- Perspectivas
Sumário

- Motivação
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Nano-estruturação de superfícies - BFI

- Interação de átomos energéticos com a superfície
- Sputtering

- Parâmetros envolvidos
  - Temperatura
  - Substrato
  - Ângulo de bombardeamento
  - Tipo de íons
  - Energia de bombardeamento
  - Fluência

- Diversidade de nanoestruturas formadas
Nano-estruturação de Metais

- Temperature Dependence

Ag (110), Ângulo: 0°  t:15 min  Gás: Ar  Eí: 1 keV

Nano - structuration of metals

Substrates

180 K, 70°, 10 min, Ar+, 1 keV

Nano-structuration of metals

Bombarding Angle

SS316L: Room Temperature, 15°, 30min, Xe+, 1keV

Policrystal

Cucatti S, Alvarez F Mat. Chem. Phys (2014), Submitted
Nano-estruturação de semicondutores

- Fluência

Substrato: Si          Gas: Kr
E_i: 2 keV

<table>
<thead>
<tr>
<th>Fluência</th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 min</td>
<td>φ=3.4x10^{17} ions cm^{-2}</td>
<td>φ=1.1x10^{18} ions cm^{-2}</td>
</tr>
<tr>
<td>10 min</td>
<td>φ=1.1x10^{18} ions cm^{-2}</td>
<td>φ=6.7x10^{18} ions cm^{-2}</td>
</tr>
<tr>
<td>60 min</td>
<td></td>
<td>φ=1.3x10^{19} ions cm^{-2}</td>
</tr>
<tr>
<td>120 min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2 μm × 2 μm

Cornejo, dissertation (2011)
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Bombardeamento com feixe de íons

Íon incidente

fase Amorfa
~2 nm

Sputtering (curvatura)

Mecanismos de...
Bombardeamento com feixe de íons

- Sputtering Yield

\[
Y = \frac{3\alpha}{4\pi^2 U_0} \frac{4m_im_t}{(m_i + m_t)^2} E
\]

Teoria de Sigmund, Phys. Ver, 184 (1969)

\[\alpha \rightarrow \frac{m_t}{m_i}\]

\[U_o \rightarrow \text{Surface binding}\]

\[s(E) - \text{stopping power keV}\]
Bombardeamento com feixe de íons

- Sputtering Yield
Bombardeamento com feixe de íons

- Sputtering Yield
Bombardeamento com feixe de íons

- Modelo de Bradley and Harper – 2D

\[ \varphi = 0 \quad \text{incidência normal} \]

\[ v(\varphi, R_x) = \frac{J}{n} Y_0(0) \left\{ 1 + \frac{a}{R_x} \right\} \]

- Distribuição esférica
- Erosão mais rápida

\[ R_x < 0 \]

\[ R_x > 0 \]

- \( R_x \) - Alcance médio de penetração dos íons
- \( J \) - Fluxo de íons incidentes
- \( n \) - Densidade de átomos do substrato
Bombardeamento com feixe de íons

- Modelo de Bradley & Harper- 3D

\[ z = h(x, y) \]

\[ \frac{\partial h(x, y)}{\partial t} = -v_0 + \frac{\partial v_0}{\partial \theta} \frac{\partial h}{\partial x} + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} - K \nabla^4 h \]

Incidência não-norma

- Taxa erosão superfície plana
- Migração dos ripples
- Sputtering dependent e da curvatura
- Difusão superficial adatomos

\[ v_0 = v_0(\theta) \]
\[ \varphi = \theta + \frac{\partial h}{\partial x} \]
Bombardeamento com feixe de íons

Falências do modelo B-H

- Longos tempos tem saturação e efeitos não lineares que não explica o modelo- Fluência.
- Válido também para superfícies lisas.
- Influência de impurezas

- Outros modelos explicam os efeitos de ordem maiores e não lineares.
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Experimento

- Motivação e Objetivo

AFM

SEM

Barreira

Carpete de nanotubos alinhados

Substrato nano-estruturado

93
Experimento

- Resultados

- Substrato: Si
- Íons: Xe
- Energia: 500 eV

Ziberi et al.
Experimento

- Rugosidade

![Graphs showing the relationship between RMS roughness and incidence angle for Xe+ and Ar+ ions on Si(100) polished surfaces.](image)

Ziberi, 2009
Experimento
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- O experimento
- Perspectivas
Perspectivas

Fluxo de átomos de Ni

500 nm
OBRIGADA!
Nano-Structures on Gallium Antimonide: Ar$^+$ Ion Sputtering

4x10$^{17}$ cm$^{-2}$, 40 s

2x10$^{18}$ cm$^{-2}$, 200 s

4x10$^{18}$ cm$^{-2}$, 200 s

GaSb

Hexagonal Symmetry

500nm

Dual Ion Beam Sputtering, 2keV

Θ~73°

Fluences: 5.2x10$^{31}$/nm2; Tempo: 90 min and \( \lambda = 37 \text{--} 43 \text{ nm} \)

M. Joe, APPLIED PHYSICS LETTERS 91, 233115, 2007
Xe\(^+\) Patterning: Experiment

Material: SS 316, Policrystal (austenite)
TiN + Ni Particles Ion Beam Deposition

Nickel Particles
- 750°C
- 1.5 min deposition
- 5 min annealing

Ni Atoms Flux
谢谢