Building College-University Partnerships for Nanotechnology Workforce Development

Physical and Chemical Vapor Deposition
Outline

• Plasma Deposition Introduction
• Deposition Coverage
• The Six Basic Steps of Chemical Vapor Deposition
• Film Growth
• Issues Concerning PECVD Deposition
• Types of PECVD Deposition
Plasma Deposition Introduction

• Plasma processing can be used to:
  – Deposit material (PECVD)
  – Remove material (etching, ashing, etc.)
  – Modify the surface through bombardment
  – Chemically modify the surface

• These scenarios are complex chemical processes

• Generally these consequences occur during any planned process, but the recipes are designed to have one result dominate
Plasma Enhanced Chemical Vapor Deposition

- The deposition of films using plasma offers the unique combination of low temperature and good film composition and coverage
- Some PECVD systems have the ability to etch and clean the substrate prior to deposition, reducing contamination
Plasma Deposition Introduction

- RF power is used to break up gas molecules in a vacuum
- Molecular fragments (radicals) readily bond to other atoms to form a film at the substrate’s surface
- Gaseous by-products are removed by the vacuum pumping system
- The substrate may be heated to increase surface reactions and drive out contaminants
Outline

- Plasma Deposition Introduction
- Deposition Coverage
- The Six Basic Steps of Chemical Vapor Deposition
- Film Growth
- Issues Concerning PECVD Deposition
- Types of PECVD Deposition
Deposition Step Coverage

• A key quality issue in deposition is step coverage
  – The thickness of a deposited material over features relative to the thickness on the top surface
Step Coverage

Sidewall Step Coverage = \(100 \times \frac{a}{b}\) (%)
Bottom Step Coverage = \(100 \times \frac{d}{b}\) (%)
Conformality = \(100 \times \frac{a}{c}\) (%)
Deposition Uniformity

• Insuring uniform coverage
  – The substrate chuck is heated to control the morphology of the deposition
  – Plasma ion bombardment is also used to increase the mobility of adatoms
Outline

• Plasma Deposition Introduction
• Deposition Coverage
• The Six Basic Steps of Chemical Vapor Deposition
• Film Growth
• Issues Concerning PECVD Deposition
• Types of PECVD Deposition
Chemical Vapor Deposition Model

1. Vapor (bulk gas) diffusion
2. Adsorption of film precursor
3. Surface diffusion
4. Nucleation and island growth
5. Desorption of reaction products
6. Diffusion of reaction products into the bulk gas
1. Precursor diffusion
2. Adsorption of film precursor
3. Surface diffusion
4. Nucleation and island growth
5. Desorption of reaction products
6. Diffusion of reaction products into the bulk for pump out

Stagnant layer

“Gas phase nucleation”

Reactant 1
Reactant 2
Byproduct of Reaction

Film growth

Public Domain: Image Generated by CNEU Staff for free use
www.nano4me.org

© 2018 The Pennsylvania State University

Physical and Chemical Vapor Deposition 12
Outline

• Plasma Deposition Introduction
• Deposition Coverage
• The Six Basic Steps of Chemical Vapor Deposition
• Film Growth
• Issues Concerning PECVD Deposition
• Types of PECVD Deposition
Forming a Film

• Given enough time and surface mobility, a deposited film grows in three stages
  – Nucleation
  – Island growth
  – Coalescence
Nucleation

- The first stage of thin film growth where clusters of stable nuclei are formed on the substrate’s surface
Island Growth

• The second stage of thin film growth where stable nuclei grow into larger island clusters based on surface mobility and density
Coalescence

• The final stage of thin film growth where island clusters coalesce, or combine, eventually forming a continuous film
Outline

• Plasma Deposition Introduction
• Deposition Coverage
• The Six Basic Steps of Chemical Vapor Deposition
• Film Growth
• Issues Concerning PECVD Deposition
• Types of PECVD Deposition
Quality Issues in CVD

• Film Density
• Film Stress
• Included Contaminants
• Surface Damage
Advantages of PECVD

• Lower processing temperature (~150 to 450°C), gives a wide range of applications
• Excellent gap-fill for high aspect ratio gaps (low density plasma)
• Good film adhesion to the substrate
• High deposition rates
• Can have high film density due to few pinholes and voids
PECVD Limitations

• Besides the expected substrate damage due to ion bombardment, PECVD has a tendency to create voids in trenches
• Void creation is a function of Mean Free Path

Key-hole defect
Voids and MFP

Balanced mean free path, rapid surface migration

Long mean free path, no surface migration

Short mean free path, no surface migration
Plasma Deposition and Photoresist

- Unlike etching, photoresist is undesirable for plasma depositions
  - Besides thermal flow due to a heated substrate chuck, plasma will react with the photoresist resulting in a volatile product that contaminates the film
Plasma Deposition and Photoresist

Photoresist reacting with plasma

Contaminated film

PR Deposited Film PR

Film

Substrate
Outline

• Plasma Deposition Introduction
• Deposition Coverage
• The Six Basic Steps of Chemical Vapor Deposition
• Film Growth
• Issues Concerning PECVD Deposition
• Types of PECVD Deposition
# PECVD Films

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysilicon</td>
<td>Used as a gate material in semiconductor devices, and as a flexible material for MEMS</td>
</tr>
<tr>
<td>Silicon Nitride</td>
<td>Diffusion barrier</td>
</tr>
<tr>
<td>Silicon Dioxide</td>
<td>Dielectric layer</td>
</tr>
<tr>
<td>Borosilicate glass</td>
<td>BSG</td>
</tr>
<tr>
<td>Phosphosilicate glass</td>
<td>PSG</td>
</tr>
<tr>
<td>Boro-phospho-silicate glass</td>
<td>BPSG</td>
</tr>
<tr>
<td>Tungsten(W)</td>
<td>Used for via fill or barrier metal</td>
</tr>
<tr>
<td>Copper(Cu)</td>
<td>Replacing aluminum as metal conductor in devices</td>
</tr>
</tbody>
</table>
Polysilicon PECVD

• Polysilicon contains many small single-crystal regions separated by grain boundaries

• Doped polysilicon serves as a gate electrode in MOS devices

• Polysilicon is also popular as a flexible material for MEMS applications
Polysilicon PECVD

- Polysilicon is deposited in PECVD by a decomposition reaction
- Silane ($\text{SiH}_4$), upon exposure to RF, decomposes into solid silicon and hydrogen gas
- The substrate chuck is heated to above 580°C to insure the proper polycrystalline structure is realized

$$ \text{SiH}_4 \ (\text{gas}) \rightarrow \text{Si} \ (\text{solid}) \ + \ 2\text{H}_2 \ (\text{gas}) $$
Nanocrystalline Silicon (nc-Si)

- nc-Si has small grains of crystalline silicon within the amorphous phase
- The grains are less than 100nm
- Behaves like a discrete gap semiconductor
- nc-Si has electron mobility much greater than that of amorphous silicon (a-Si)
- Has found use in solar cells due to its strong light absorption properties
Silicon Nitride PECVD

• Nitride is used as:
  – A final passivation layer on chips for scratch protection
  – A moisture barrier
  – Radiation shielding
  – A barrier against Na diffusion

• PECVD nitride contains hydrogen (9-30%), this can degrade the film

• PECVD nitride is also exposed to greater compressive stress due to ion bombardment, causing voids and cracks in underlying layers
# Silicon Nitride: PECVD VS LPCVD

<table>
<thead>
<tr>
<th>Property</th>
<th>LPCVD</th>
<th>PECVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Temperature (°C)</td>
<td>700 to 800</td>
<td>300 to 400</td>
</tr>
<tr>
<td>Composition</td>
<td>$\text{Si}_3\text{N}_4$</td>
<td>$\text{Si}_x\text{H}_y\text{N}_z$</td>
</tr>
<tr>
<td>Step Coverage</td>
<td>Fair</td>
<td>Conformal</td>
</tr>
<tr>
<td>Stress at 23°C on silicon (dynes/cm²)</td>
<td>1.2-1.8 x 10^{10} (Tensile)</td>
<td>1-8 x 10^{9} (compressive and tensile)</td>
</tr>
</tbody>
</table>

Andrzej Mieckowski Penn State Nanofabrication Facility
Silicon Nitride PECVD

• PECVD nitride is formed by reacting silane with either ammonia (NH$_3$) or nitrogen(N$_2$)
  – Using N$_2$ reduces the amount of hydrogen in the film, but is difficult to dissociate.
• SiH$_4$(gas)+NH$_3$(gas)$\rightarrow$Si$_x$H$_y$N$_z$(solid)+H$_2$(gas)
• SiH$_4$(gas)+N$_2$(gas)$\rightarrow$Si$_x$H$_y$N$_z$(solid)+H$_2$(gas)
## Example Nitride PECVD Recipe

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (Sec)</th>
<th>Pres (Torr)</th>
<th>Cham Temp (°C)</th>
<th>Subs Temp (°C)</th>
<th>Power (W)</th>
<th>N₂ (SCCM)</th>
<th>NH₃ (SCCM)</th>
<th>SiH₄ (SCCM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>4.0</td>
<td>410</td>
<td>325</td>
<td>0</td>
<td>4000</td>
<td>275</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4.0</td>
<td>410</td>
<td>372</td>
<td>500</td>
<td>4000</td>
<td>275</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>4.25</td>
<td>410</td>
<td>353</td>
<td>640</td>
<td>4000</td>
<td>100</td>
<td>285</td>
</tr>
<tr>
<td>4</td>
<td>44</td>
<td>4.25</td>
<td>410</td>
<td>379</td>
<td>640</td>
<td>4000</td>
<td>100</td>
<td>285</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.3</td>
<td>410</td>
<td>377</td>
<td>50</td>
<td>2500</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.3</td>
<td>410</td>
<td>375</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Andrzej Mieckowski
Penn State Nanofabrication Facility
Silicon Dioxide PECVD

- Oxide is formed by reacting silane (SiH$_4$) with either oxygen (O$_2$), nitrous oxide (N$_2$O), or carbon dioxide (CO$_2$) in a plasma.
- Oxide can also be doped with boron (B$_2$H$_6$) or phosphorous (PH$_3$) to form BSG or PSG respectively.
Silicon Dioxide PECVD

• $O_2$ is generally not used due to its ability to readily react in the gas phase, generating particles that promote poor film quality
• $N_2O$ is the preferred reactant due to its ability to produce a higher quality film
• $SiH_4(gas) + 2N_2O(gas) \rightarrow SiO_2(solid) + 2N_2(gas) + 2H_2(gas)$
Tungsten PECVD

• Tungsten is a refractory metal (mp = 3410°C) widely used in multilevel metal structures as an interconnect and a barrier metal

• Tungsten qualities
  – High conductivity
  – Excellent thermal capabilities
  – Good CVD step coverage
Tungsten PECVD

• Tungsten deposition via PECVD is a fairly simple process
• Tungsten hexafluoride \((WF_6)\) reacts with hydrogen to form solid tungsten and hydrofluoric acid vapor

\[
WF_6(gas) + 3H_2(gas) \rightarrow W(solid) + 6HF(gas)
\]
Copper PECVD

• Copper is replacing aluminum as the metal conductor of choice in high speed devices

• Copper qualities
  – Excellent conductivity
  – Low production cost
  – Good step coverage
Copper PECVD

- Copper PECVD is the most common method of deposition
- The metal organic bis-hexafluoroacetyl-acetonate-Cu$^{II}$, written as Cu(hfac)$_2$ is placed into the system in powder form and is mixed with hydrogen gas and then vaporized and carried into the reaction chamber

$$\text{Cu(hfac)}_2 + \text{H}_2 \rightarrow \text{Cu} + 2\text{H(hfac)}$$