Integrated ESH Assessment: Cu CVD and ALD
Unit Process Optimization (Thrust C, Task C-5)

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Strategic Plan

New Chemistries and Processes
- New BE processes / new low-k
- New HE processes / new high-k
- New patterning processes
- New water purification processes

Use Reduction
- CMP waste reduction
- Low chemical surface prep
- Low-water rinse processes
- Low-energy processes

Reuse and Recycle
- Chemicals recycle and reuse
- Water recycle and reuse

Abatement and Discharge Control
- Novel plasma reactor abatement
- CMP waste treatment
- Waste water treatment

Thrust A  Thrust B  Thrust C  Thrust D

Integrated ESH Assessment

Deliverable  Major Deliverable  Testbed

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**Perspective**

- **Project Objectives**
  - Exploit physics-based dynamic simulation to extract ESH metrics as function of equipment design and process recipe
  - Focus on Cu CVD and ALD processes as unit process demonstration testbed for methodological approach

- **ESH Impact**
  - Development and demonstration of methodology for integrated ESH impact assessment
  - Fusion and synergy between multiple metrics: ESH, manufacturing, and technology

- **ESH Metrics**
  - Mass balance
  - Energy balance
  - Other metrics for manufacturing efficiency and technology performance relevant to tradeoff analysis with ESH
Dynamic Simulator

Multi-level Hierarchical Structure

User-friendly Pop-Up Panels for Real-Time Process & Equipment Parameters Control

Real-Time Monitoring of the DYNAMIC Behavior of Equipment, Process, & Control System through Process Cycle

Real-Time Monitoring of the DYNAMIC and INTEGRATED Behavior of Manufacturing Efficiency & ESH Assessment Metrics

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Blanket Cu CVD Process

\[ 2 \text{Cu}^I(\text{hfac})(\text{tmvs}) \rightarrow \text{Cu}^0 + \text{Cu}^{II}(\text{hfac})_2 + 2(\text{tmvs}) \]

PROCESS CONDITIONS FOR SIMULATION

Substrate Temp 150 - 250°C (180 - 200°C), Vaporizer, Gas Lines and Chamber at 60-65°C. Ar/He CarrierGas Flow 50 – 500 sccm (100 sccm)

CupraSelect™ Liquid Flow
0.1 – 0.25 cc/min (for seed 200 - 500 A), up to 2.5 cc/min (for fill 200 - 500 nm)

Available as Schumacher CupraSelect™ Liquid at R.T.

tmvs = trimethylvinylsilane C₅H₁₂Si
hfac = hexafluoroacetylacetonate dihydrate C₃HF₆O₂

Delivered to the showerhead using DLI system.

Cu CVD Dynamic Behavior
Dynamic behavior of process and equipment through the process cycle is revealed by simulator

Cu CVD Time-Integrated Behavior
Signals integrated through complexity of the detailed process cycle can determine environmental metrics
Cu CVD Mass Balance Optimization

High temperature & high pressure reduce cycle time

High temperature & high pressure increase utilization efficiency

win-win region for cycle time and utilization
Cu CVD Mass Balance Optimization

- Higher flow rate: Shorter cycle time
- High temperature and high flow rate reduce cycle time
- High temperature and low flow rate increase utilization rate
- Flow rate forces tradeoff between cycle time and utilization rate
- Higher temperature
- Higher utilization

Higher flow rate (ccm/s ccn)
Flow rate (ccm/s ccn)
0.5/100
1.5/300
2.5/500
0.00
Cycle Time (Min)

Temperature (°C)

Utilization rate (%)

Higher temperature and high flow rate reduce cycle time.
Cu ALD Processes

Reaction Chemistry

(A) \( Cu(hfac)_2 \rightarrow Cu + (hfac)_2 \)

(B) \( 2(hfac)_2 + H_2 \rightarrow 2(H-hfac)_2 \)

"Dynamic" ALD reactor:
continuous reactant flow throughout the process cycle;

Continuous reactant flow during exposure cycles, not at all times in process (e.g. purge)

ALD process normally has longer cycle time and lower utilization compared with CVD

Can we really say this? We don't have consistent sticking coeff's in ALD cf. dep rates in CVD.
Cu ALD Reactor Design: “Stagnant” Reactor

“Stagnant” ALD reactor: Reactant flow only up to certain amount reactant input. Then reactant is held within ALD chamber until cycle finishes.

- **Cu(hfac)$_2$ exposure**
  - Reactor
  - 10$^{-5}$-6 torr

- **Flushing**
  - Reactor
  - H$_2$ exposure
  - 10$^{-5}$-6 torr

- **Sampling**
  - Wafer
  - Cu (hfac)$_2$
  - Substrate heater

Why 10 mtorr here but 500 mtorr in previous dynamic ALD?

Do we know that stagnant isn’t already known and used elsewhere?

Concept of “Stagnant” ALD reactor being developed in U. Maryland
Cu ALD Process Modes

“Stagnant” Reactor can achieve both larger utilization and shorter cycle time compared with “Dynamic” Reactor

“Stagnant” Reactor

“Dynamic” Reactor

Here presumably all the parameters are same for dynamic and stagnant

Where do the cycle times come from? I don’t see them in the data. What physical parameter determines end point of cycle time?
Analysis in ALD Process

Longer Cu(hfac)$_2$ cycle time will increase Cu(hfac)$_2$ surface coverage, longer H$_2$ cycle time will decrease the un-desorbed (hfac) ligand:

(hfac): Hexafluoroacetylacetonate dihydrate $C_3HF_6O_2$

More (hfac) remains, more impurity content in Cu film

Trade-off between two manufacturing metrics: Cycle Time & Film Quality

Win-win between manufacturing and ESH metrics: Cycle Time & Utilization

I don’t understand this chart. C incorporation should depend on exposure times of both species, in a simple model at least. There must be some relation between the two exposure times built in.
CVD/ALD Reactor Power Sources
- Pareto Analysis

Sources of Energy Use:
Substrate Heater, Process Pumps, Process Chamber, Vaporizer & Gas Lines Heating, DLI System Pumps, Pre-Heated Precursor, Process & Equipment Control Units, PC’s, etc.

<table>
<thead>
<tr>
<th>Sources of Energy Use</th>
<th>Power (KW) per Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump Package</td>
<td>3.26</td>
</tr>
<tr>
<td>MFC</td>
<td>0.0267</td>
</tr>
<tr>
<td>DLI</td>
<td>0.2</td>
</tr>
<tr>
<td>Heated Valve</td>
<td>0.03</td>
</tr>
<tr>
<td>Pressure Gauge</td>
<td>0.005</td>
</tr>
<tr>
<td>RF Power</td>
<td>0.5</td>
</tr>
<tr>
<td>Programmable Controller</td>
<td>0.15</td>
</tr>
<tr>
<td>Exhaust Valve Controller</td>
<td>0.05</td>
</tr>
<tr>
<td>PC</td>
<td>0.2</td>
</tr>
<tr>
<td>Substrate Heater</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Data sources:
1. Leybold Vacuum Product Inc.
2. MKS Instrument
3. Ulvac Technologies Inc.

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CVD/ALD Reactor Power and Energy

**Substrate Heater:**
- Heater kept at high temp at all times
- Radiative Heat Loss ~ \((T_2)^4\)
- Conductive Heat Loss ~ \((T_2 - T_1)\)

**Pump Package:**
- Pumps kept running at all times ➔ significant energy consumption
- Pump power is a function of pump inlet pressure ➔ power difference during process time and pump-out time

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Pump system is the dominant energy consumption source in Cu CVD and ALD process
Utility Function Analysis

- Tradeoff situations pose a common and substantial challenge
  - Here, increasing flow rate reduces materials utilization while improving cycle time
- QUESTION: how do we combine these very dissimilar metrics?
- ANSWER: systems engineering tells us to define a utility function that depends on the different metrics, e.g. the example in the expression above
- Calculate Utility for various $\alpha/\beta$
- Note that Utility is optimized at low flow rate for small $\alpha/\beta$ (where utilization is primary determinant of Utility), and correspondingly for the other case
- Defining a meaningful Utility function is a major challenge

$$\text{Value} = \alpha \times \frac{1}{\text{Cycle Time}} + \beta \times \text{Utilization}$$
Utility functions for ESH impact assessment should include:
- Economic factors, determined as COO
- Environmental factors, addressing in-fab and direct upstream and downstream consequences of in-fab practice

These link to UCB and MIT activities
- EnV-S analysis of ESH COO
- MIT assessment of upstream multipliers on in-fab process choices
Future Plans & Industrial Interactions

**Cu CVD process**
- Continue analysis of ESH & Manufacturing metrics
- Improve model if appropriate

**Barrier layer process (UMd)**
- Develop dynamic simulator for ultrathin barrier CVD & ALD with mass & energy metrics
- Carry out initial ESH assessment

**Tele-seminars**

**Collaborations begun with NIST National Semiconductor Metrology Program**
- Experiment & Modeling
- Cu CVD
- Barrier layer CVD & ALD

**Transfer Cu CVD simulation to SimPLE framework for learning systems**
Conclusion

• Cu CVD and ALD unit process models were established and used to assess ESH metrics, modeling approach provides platform for manufacturing and environmental metrics optimization analysis

• Evaluation of mass balance reveals clear tradeoffs between competing manufacturing and ESH metrics, and even within manufacturing metrics
  – *Must deal with constructing sensible utility functions*

• ALD reactor design is essential to improve manufacturing and ESH metrics
  – *“Stagnant” ALD reactor is more desirable than conventional “dynamic” reactor*

• Pump system is the dominant component of energy consumption in both Cu CVD and ALD System
  – *Opportunity for improvements in concert with component suppliers*
  – *(Not all technical factors in pump choice yet addressed)*

• Economics and environmental perspectives drive different components of ESH assessment
  – *Economics (COO) in the fab*
  – *Environmental coupling to mass and energy consequences directly relating to in-fab practice*
BACKUP – LAST YEAR SITE REVIEW
Project Scope

**Levels**
- **Systems**
  - Aggregation
  - Optimization
  - Decision support
- **Architecture**
  - Sequences
  - Component populations
  - Operations algorithms

**Components**
- Process tools
- Infrastructure elements

**Systems**
- EnV-S analysis
- Decision & quantification shell

**Architecture**
- EnV analysis
- Architecture shell

**Components**
- Process modeling shell & database

**MetRICS**
- EnV-S analysis
- Decision & quantification shell
- Process modeling shell & database

**Technology**
- Mat’s & dev perf
- Yield
- Reliability

**Manufacturing**
- Throughput, cycle time
- CoO
- Risk

**ESH**
- ESH-CoO
- Envir beyond fab
- Health
- Safety

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Dynamic Simulation at the Unit Process Level

**Unit Process:** Simulation tools to generate manufacturing & ESH metrics

- **Static & Dynamic models & simulators to represent the time-dependent behavior of processes & equipment**

### Time-integrated

**PROCESS RECIPE**
- Recommend Optimal Chamber Press

**EQUIPMENT SIMULATOR**
- Thruputs, Residence Time, Gaseous Species Concentrations, Total & Partial Pressures, Wafer Temp – all vs. Time
- Reactant Consumption, Gaseous Rxn By-Products Generation as a func of Time
- Real-Time Film Thickness Control

**PROCESS SIMULATOR**
- DYNAMIC Deposition Rate, Film Thickness – vs. Time

**MANUFACTURING & ESH METRICS**
- INTEGRATED Mass Balance, Reactant Utilization, Cycle Time, Power required, Energy expended (per unit thickness)

See Demo
Mass & Energy Balance

**Blanket Cu CVD**

*example shown for*

40 Torr, 250°C, Precursor 2.5 ccm, Carrier Gas 500 sccm, total cycle time of 2.32 min to grow 5000 A

on a single 300 mm wafer

- Mass & Energy Balance obtained by dynamic simulation thru process cycle for any chosen process recipe & system design

- Cu Film Deposited 4.49E-7 kg/cm²
- Cu I Precursor 9.54E-7 kg/cm²
- Carrier Gas (Ar) 1.60E-6 kg/cm²
- Cu(II)(hfac)₂ 3.03E-6 kg/cm²
- tmvs 1.41E-6 kg/cm²

(assuming known chemistry – slide 6)
Blanket Cu CVD Process

2 Cu^I(hfac)(tmvs) → Cu^0 + Cu^II(hfac)_2 + 2(tmvs)

Available as Schumacher CupraSelect™ Liquid at R.T.

tmvs = trimethylvinylsilane C_3H_7Si
hfac = hexafluoroacetylacetonate dihydrate C_3HF_6O_2
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RANGE OF PROCESS CONDITIONS FOR SIMULATION EXPERIMENTS

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CupraSelect™ Liquid Flow
0.1 – 0.25 cc/min (for seed 200 - 500 A)
up to 2.5 cc/min (for fill 200 - 500 nm)

Max Chamber Pressure Defined by DLI Physics
In general, < 10 Torr (for seed) & < 4 Torr (for blanket fill) for low CarrierGas Flow Rate (50-100 sccm), and Higher Pressures for higher CarrierGas Flow Rates (upto 500 sccm)

simulation model incorporates details of known process chemistry

"ARRHENIUS PRESS CURVE" SIMULATION – Pressure-dependence of Growth Rate at fixed Temp & Flow Rates

"ARRHENIUS CURVE SIMULATION" – Effective Rate of Rxn composed of Transport-limited & SurfaceRxn-limited Regimes

Growth Rate (A/min)

10000

1000

100

10

1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0

1000/WaferTemp(K)

Growth Rate (A/min)

10000

1000

100

10

0 5 10 15 20 25 30 35 40 45 50

Press (Torr)
Dynamics of Manuf & ESH Metrics

Graphs showing various metrics such as Press (Torr), Temp (°C), Growth Rate (A/min), Film Thickness (Å), Power (W), Energy (J), and Precursor Utilization (%). The graphs illustrate the dynamics of manufacturing and environmental sustainability metrics.
Cu CVD Co-Optimization for Manuf & ESH

- High Press, High Temp → Win-Win Situation for Cycle Time & Utilization

In the case of

**CyCle TIme**
- Manufacturing

&

**Reactant Utilization**
- ESH & Manuf

PRESS: 5, 10, 20, 30, 40 TORR
TEMP RANGE: 150 – 250°C
CONST FLOW RATES 1 CCM / 200 SCCM

Higher Temperature win-win region for cycle time and utilization

In the case of

**150°C**

2.5/500 (707 sccm)

**170°C**

Higher Flow Rate

**190°C**

0.5/100 (141 sccm)

**210°C**

2.5/100 (141 sccm)

**230°C**

2.5/200 (141 sccm)

**250°C**
Cu CVD Energy Optimization

Simulation
- Power required to maintain wafer temp
- Energy expended per 500nm Cu deposited at that temp

Higher temp requires more heating power

Radiation ($\sim T^4$) and conduction ($\sim \Delta T$) are both important heat transfer mechanisms

ENERGY OPTIMIZATION
Growth Rate rises exponentially with temp
(Arrhenius behavior, thermally activated)

AT 5 TORR, CONST FLOW RATES
1 CCM / 200 SCCM

Power(W), Energy(J)

Power required to maintain wafer temp
Energy expended per 500nm Cu deposited at that temp

Radiation ($\sim T^4$) and conduction ($\sim \Delta T$) are both important heat transfer mechanisms.