Use of Multiphysics modeling to improve solar thin film performance and manufacture

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Abstract

Solar and wind energy are gaining attention for both technology innovation and commercialization, due to the environmental impacts of conventional energy sources, lack of technology breakthrough with hydrogen based systems, and rising oil prices. Among solar energy technologies, thin film photovoltaic systems promise greater cost effectiveness, but they require significant improvement in conversion efficiency, packaging, scale-up in manufacturing and quality control. On the other hand, Siemens and Ethil processes are well established methods for polysilicon manufacturing for solar grade silicon. Multiphysics modeling, which includes effects of fluid flow, heat/mass transfer, electric fields, etc., provides valuable insight to achieve these improvements.

Introduction

According to the current estimates by Energy Information Administration of United States Department of Energy, (Ref: http://www.eia.doe.gov/oiaf/ieo/highlights.html), although solar energy production and consumption globally has not reached any measurable proportion, the prognosis of significant solar capacity within next 10 years looks very promising based on the initiatives and will power of the governments across the globe. Three major barriers in solar energy production and usage scale-up are:

a) Conversion efficiency and life (infrastructure, economics)
b) Raw materials and production technologies (process innovation, productivity and cost)
c) Storage and distribution (battery technology, off-/on-grid flexibility)

Significant progress has been made and several promising technologies are being commercialized for each of these components. But competitiveness in terms of economic viability of solar equipment capital cost and durability compared to conventional societal and industrial energy usages, life styles, and balance of supply and demand is yet to be established. Commercialization initiatives in these areas require cost-effective technology evolution and operational scale-up in sync with each other. For example, crystalline structures of solar grade metals (silicon, and various alloy systems of copper, indium, gallium, selenium, cadmium and tellurium) are critical for defining all aspects of the solar energy industry namely materials production processes, to wafer making, processing, solar cell packaging, panel assemblies, electronic off-/on-grid switching, storage and distribution technologies. Government initiatives in these respects are providing both cooperative connectivity, as well as basic impetus for fundamental inventions [http://www.nrel.gov/solar/, http://ec.europa.eu/energy/, and similar agencies around the globe]. Entrepreneurial initiatives are also realizing the need to expedite the commercialization initiatives in various stages of this evolving energy supply chain. In this paper, we focus on reviewing the core engineering and scientific components which provide the platform solutions for both understanding the physics and chemistry of the solar photovoltaic materials and equipment as well as on the aspects of scalable manufacturing of such solar grade materials and equipment.

It is widely recognized that the impurity levels that can be accepted in solar grade silicon are higher than for electronic grade silicon, where impurities must be below the ppb level. The drivers are both cost and balance of demand and supply in the market place. Consequently, each of the parallel technologies, like multi-crystal (MC) silicon ingots, edge-defined film growth wafers, and other thin films including chemical vapor deposition (CVD) based deformable films and plasma-enhanced CVD techniques, requires analysis of corresponding thermo-physical processes and evolution of the morphologies like segregation, grain boundaries, and dislocations. Further more, specific analyses are needed to understand the core strengths and weaknesses of each process in order to successfully compare economics of consistent production scale-up initiatives. For example, ability to economically manufacture of solar grade MC granules from metallurgical grade silicon appears attractive compared to Siemens process. Such granules require both densification as well as mixing with wafer residues from Czochralsky crystals prior to directional solidification. Much of the downstream processing technology remain very similar to the EG silicon processing. Similarly, not many industrial scale solar MC silicon manufacturers have mastered the control of fines and overall productivity in the Fluid Bed reactor technology (Ethil process). Most importantly, most of these existing technologies require one or more secondary purification steps and hence thin film technologies appear attractive from viewpoint of manufacturing and custom cell shapes and sizes. However, the technology challenges associated with thin films include process stability and consistency during scale-up as well as efficiency and life issues of the end products.

The challenges in the materials and process innovations on photovoltaic technologies are being addressed increasingly by simulation technologies for obvious advantages of greater insight, shorter overall development time and availability of various tools to carry out the Simulation Driven Product and Process Development initiatives. The core challenges in the process innovation are the multi-step dynamics of purification, wafer making, cleaning, etching, gettering, doping, sealing, coating, and various other sub steps and the need for compatibility and consistency along the way. Since the molecular and even electron level behavior dictates the consistency (or the lack thereof) in the process or final product quality, the problems are also multi-physics and multidisciplinary in nature. In this paper, instead of addressing any particular vertical process in the manufacturing of a particular PV material, analysis methodologies for various subcomponents are discussed. In this context, the similarities between techniques used for high-purity electronics materials manufacture and processes used for solar materials (with their relatively less stringent purity requirements) are acknowledged. Similarly, the Fluid Bed reactor technology has significant similarity with the bulk and specialty chemical manufacturing processes involving gas phase catalytic conversion of hydrocarbon derivatives – the similarity extends to even the need to deal with the fines formation and controls. The alloy solidification processes share the same physics that are essential to predict segregation of alloying elements in directional solidification of precious metals. For crystal growth processes, melting, solidification, natural convection and radiation are analyzed and optimized with simulation. In terms of film growth technologies, simulation technologies as applied to CVD and other processes for semiconductor industry are equally applicable.

Tungsten CVD

The tungsten chemical vapor deposition (CVD) is a key process used to fabricate reliable contacts and interconnects in manufacturing semiconductor devices. In the CVD process, tungsten is deposited on the wafer as a planar film and then selectively removed from the surface so that tungsten plugs remain [1]. Computational fluid dynamics (CFD) software tools provide a fast way to examine the flow patterns, temperature and species distributions, as well as specific quantitative values, such as the tungsten film thickness variation across the wafer. Figure 1 shows the CFD results illustrating the deposition rate uniformity on wafer in a Concept Two ALTUS chamber from Novellus Systems.

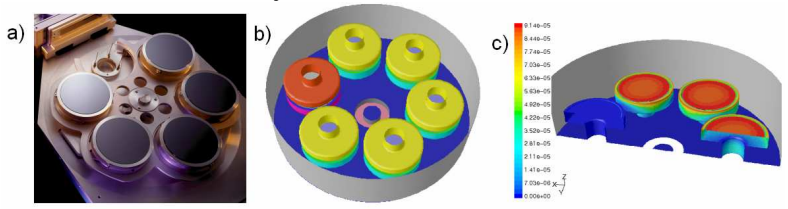

Fig. 1 Flow analysis of the Concept Two ALTUS tungsten process chamber (courtesy of Novellus Systems Inc.): a) equipment, b) 3D model and c) tungsten deposition rates

Rapid Thermal Processing

In a model of a rapid thermal processing (RTP) chamber where the radiant energy source is a plasma arc tube, the radiation is collected and focused by a highly reflective and contoured surface. The radiation passes through a transparent quartz window and is absorbed by the underside of the wafer surface and the internal walls of the chamber. Uniform heating of the wafer by the radiant energy is critical to prevent thermal stresses and warping, and to obtain uniform deposition/etch rates. The shape of the reflector surface must be carefully designed to achieve this goal. The exact shape of the reflector is incorporated into the CFD model [2] and the resulting radiant energy distribution is calculated. If the uniformity is found to be unacceptable, the shape of the reflector can be adjusted in the model until it provides satisfactory results.

Another factor having influence on the radiant energy distribution is the quartz window. The orientation, thickness, location and material properties of the window cause the radiation to be distorted as it passes through the window. This refraction/reflection is calculated by the CFD program using Snell's law – the net influence will be seen on the wafer irradiation uniformity. Figure 2 shows temperature distributions near the plasma arc tube in an RTP chamber.

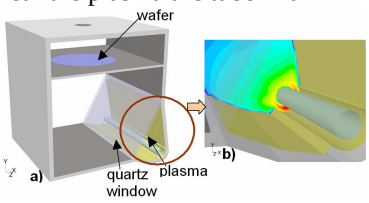

Fig 2 Virtual prototype of an RTP system: a) 3D solid model of RTP chamber, b) CFD results showing temperature contours near the plasma arc heat source.

Photoresist Application

Spin coating is widely used to apply photoresist material to wafer surfaces and to apply dielectric or insulating layers during microcircuit fabrication. It is a process whereby a volatile liquid is applied to the surface of a rotating substrate. The airflow distribution

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in a spin coater has a critical effect on film thickness uniformity because it strongly influences the drying rate. The airflow patterns also have a significant effect on particle contamination of the wafer. Failure to immediately remove the excess floating particles that are generated during the spin-off stage can result in contaminant deposition on the chamber walls or on the wafer. When the wafer spins, it draws air from both the top opening and the bottom gap, and forces it outward radially (Figure 3). This results in a positive pressure buildup underneath the baffle that contributes to a flow blockage and also explains why there are no recirculation zones underneath the baffle as was widely presumed. Based on CFD modeling [3] and experimental results, the spin station geometry was modified for later generation tools. The new design improved the photoresist uniformity and minimized the particulate contamination of the wafer surface.

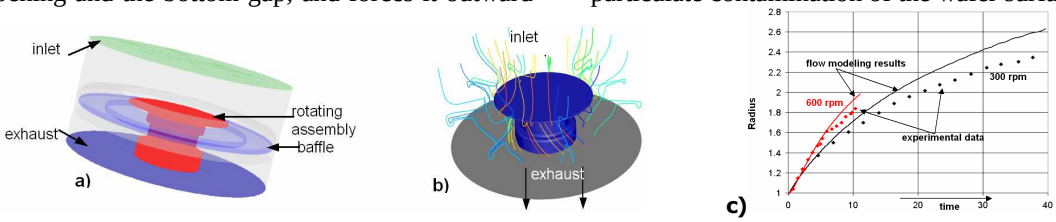

Fig. 3 CFD analysis of a spin coating station: a) 3D solid model of spin coater, b) flow path lines traced from inlet reveal the complex air flow patterns and c) Comparison of modeling and experimental data for the spreading of a liquid droplet during spin coating. Graph shows non-dimensionalized drop radius versus time for 2 different spin rates. Experimental data is from [4].

The latest work in this area goes one step further by modeling the movement of the photoresist liquid over the surface of the wafer. Figure 3c shows the good comparison of the spreading rate of a coating droplet as predicted by flow modeling and experimental results [4].

Etching

Plasma etching is an indispensable part of modern integrated circuit fabrication, where it is routinely used: to etch silicon, silicon dioxide and contact metals; to strip photoresist and masking materials; and for reactor cleaning. In reactive gas plasmas, electrons decompose the feedstock gases into radicals and ions. Because the electrons and ions react on tremendously different time scales, modeling their interaction with the flow of the neutral species is especially challenging. Recent efforts have focused on coupling transient plasma chemistry models with steady-state fluid flow simulations that include a reduced-order description of the plasma chemistry.

Figure 5a shows the argon molar density and argon ionization density distributions in an inductively coupled plasma system. The argon ionization is centered about the axis of the reactor, closely following the electron density distribution, and the simulations are able to capture this trend quantitatively [5]. Figure 5b shows the overall chamber clean rate in a P5000 reactor using fluorocarbon discharges. The simulation results indicate that at high pressures, a more spatially confined plasma is generated for cleaning the electrode region, which has the heaviest buildup of deposits. At low pressures, the plasma is more spread out allowing it to clean the more remote chamber surfaces [6, 7]. The CFD results were able to predict the trends correctly, and shed light on the change in plasma constituents with respect to process parameters.

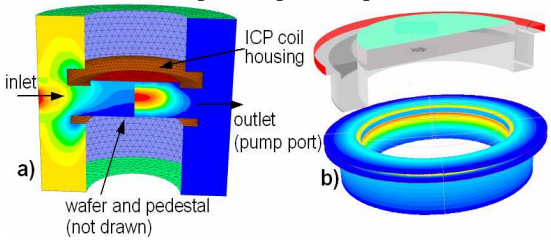

Fig. 5 a) Argon ion (left) and Ar+ (right) density distributions in a GEC reactor, and b) Applied Materials P5000 reactor model (top) and overall chamber clean rate results using C_4F_8-O_2 discharges (bottom).

Atomic Layer Deposition

Atomic layer deposition (ALD) is receiving increased attention lately because of its ability to produce ultra-thin and conformal film structures using sequential self-limiting surface reactions. Simulation of an ALD process is difficult because of periodic pulsing of reactants and purge gases in short intervals. A comprehensive model for ALD should include gas phase transport, transient boundary conditions, adsorption/desorption and surface reactions. A schematic of a typical ALD reactor is shown in Figure 6a, and the axi-symmetric geometry along with the mesh used in the CFD simulations is shown in Figure 6b. Simulations are performed for 10 cycles to predict deposition rates of TiN diffusion barriers using $TiCl_4$ and NH_3 as reactants [8]. Figures 7a and 7b shows the molar concentration distributions of $TiCl_4$, and NH_3 as a function of pulse time. The simulations show that there is no cross-contamination between the pulse cycles, and suggest that the purge time can be reduced to less than 2 seconds.

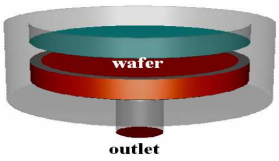

Fig 6a Showerhead geometry

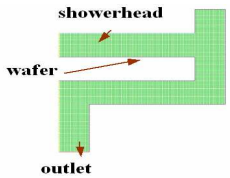

Fig. 6b The computational mesh

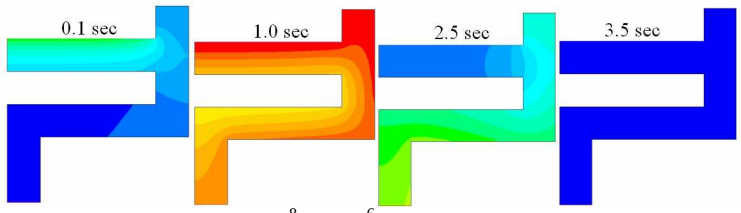

Fig. 7a Contours of $TiCl_4$ concentrations [range: 0-($5x10^{-8}$)-$1x10^{-6}$] at different pulse times

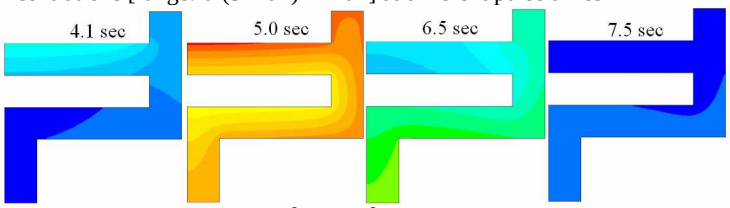

Fig 7b Contours of NH_3 concentrations at [range: 0-($5x10^{-8}$)-$1x10^{-6}$] different pulse times

Figure 8a shows the Ti and N growth rates as a function of pulse times. The simulation results predicted that the growth rates are uniform over successive ALD cycles. Figure 8b shows the predicted film thickness at the wafer center over 10 ALD cycles. The simulation results captured different growth regimes – a transient regime where film thickness for one deposition cycle increases towards a constant value, and a converged region where film thickness for a given deposition cycle is constant [9]. The CFD model provides a framework to investigate transport and growth mechanisms for compound semiconductors, SiO_2, metal oxides, and single element metal films.

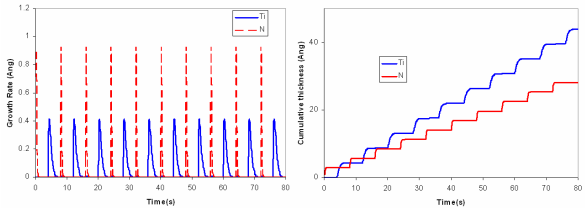

Fig. 8 a) Growth rate for Ti and N as a function of pulse length; b) Predicted film thickness at wafer center over 10 cycles

Multi-scale modeling to resolve distinct spatial and time scales

Performance of most solar cells is dependent on the structural details, followed by the textural details during both materials manufacturing and productization. For example during manufacturing, deposition and film growth during various CVD processes, gettering depth of impurities, grain-boundaries and dislocations will be mostly below the grid-scale for the regular wafer-scale physical phenomena. Similarly, product performance is dictated by the passage of energy through the passivation layers, radiation transmission, reflection, and absorption, which occur on different length-scales and depend on the wavelengths of the incident radiations. It is therefore advantageous to adopt a multi-scale modeling approach, including the use of homogenization theory whereby small-scale high-frequency variations in transport parameters are selectively resolved through the computational grids, while the sub-grid-scale fluctuations are first resolved in a finer local scale of importance and then stochastically averaged for the upper, coarser scales. In this section a basic formalism of such a multi-scale approach is discussed in the context of wafer cleaning and processing steps.

In chemical mechanical planarization (CMP) simultaneous effects of many physical and chemical phenomena (free-surface flow, mixing of two fine slurries in the presence of air, surface reaction between the slurries and the textured solid surfaces), are evident while each one is dominant in geometries that involve characteristic features in μm, mm, and cm scales – all in the same problem. In addition, for accuracy and stability reasons, the typical simulation time steps are limited to 0.1 milliseconds or smaller, making it impossible to achieve long transient analysis within reasonable calendar time, when resolving all such length scale variations in a single resolved geometry. Typically these runs involve 3-20 million finite volume cells and transient simulation for about 2 or more minutes physical flow time. The situations are very similar for etching, deposition, passivation processes. Homogenization theories [10,11,12] characterize the influence of structural details from smaller scales in terms of locally volume-averaged tensorial permeability and the effective porosity in the larger scales, together with information about other space-sensitive heterogeneous quantities (porosity,

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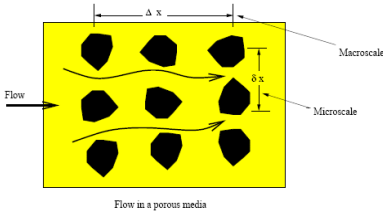
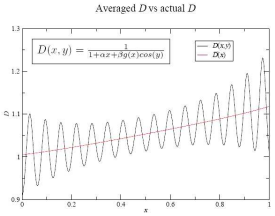
diffusivity, thermal conductivity, etc)(Figure 9). Using such multi-scale mapping techniques, a hierarchy of smaller scales can be reconstructed in the framework of the macro-scale. The macro-scale hydrodynamic framework will benefit from the zonal features of textural details for capillary driven flows, ion transport, and so on, without needing to resolve all scales through meshing at the same time.



a) Microscopic view of a porous texture



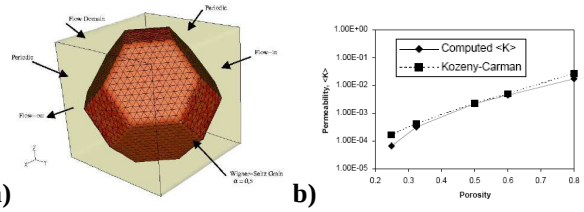
b) Small and large scale axial variation of pressure

Figure 9 Detailed views of porous media / surface flow and pressure variation

The problem is solved using FLUENT, a finite volume based CFD package for a single Wigner-Seitz grain, a polyhedron of 14 sides. Flow is modeled as laminar with density set to a low value to minimize non-linear advection effects. Results are compared against well-known Kozeny-Carman formula (1932).

$$\langle K \rangle = \frac{1}{5}\frac{n^3}{(1-n)^2}\left(\frac{V_s}{A_s l}\right)^2$$

Here K is permeability, n is porosity, V_s is the solids' volume and A_s is the solids' surface area.



a) **b)**

Figure 10 Canonical analysis of permeability for a Wigner-Seitz grain in a fluid domain; a) The geometry details and b) Comparison of Kozeny-Carmon vs. Homogenization theory based prediction of permeability

The Wigner-Seitz grain has been used as a convenient proof-of-concept example for simulating flow around a porous particulate. In general, the expectation is that canonical forms of the lower-scale geometric details can be defined through supplemental meshes which can be solved either as separately spawned coupled analyses or through a set of smaller-scale characterization runs leading to a look-up table with local coordinate system that reads in the anisotropic permeability data and applies them in the global coordinates. On the other hand, from any macro-scale transient solution, a local analysis can be spun off to capture finer space-time details. This method can be looped over multiple geometric scales simultaneously. Occasionally, due to the relative motion between contacting geometries, these vectors/tensors would have to be implemented in moving frames of reference. Multi-scale modeling is a computational framework with a wide-range usefulness including building two-way connectivity among adjacent length scales such that appropriate physics and chemistry dominant at respective scales can be interpreted duly while collecting information for understanding and optimizing engineering processes. This is a technology under progressive development at ANSYS for various energy technology areas including solar, fuel cells, and bio-fuel applications.

End note

In this work, we presented a diversity of components of Simulation Driven Product and Process Development (SD**P**D) technologies. There are several other components not touched up on due to length of the text: Solidification, film growth, plasma enhanced processing, diffusion in solids, liquid- and solidifying liquid phase equilibria, gas phase synthesis, particle size distribution are few of them. Most of these modeling technologies are matured by years of their applications in the semiconductor and specialty chemicals industries although relatively less attention was paid for photovoltaic applications. Recently, the significant advantages of SD**P**D have been applied to improve EFG, ribbon and fluid bed reactor based technologies [13, 14, 15].

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