Simulating conditions for the atomic level processing of metals

Simon D. Elliott[a,*], Jacob L. Gavartin[b], Alexandr Fonari[c]

[a] *Schrödinger GmbH, Glücksteinallee 25, 68163 Mannheim, Germany*
[b] *Schrödinger Technologies Ltd, Davidson House, The Forbury, Reading RG1 3EU, UK*
[c] *Schrödinger Inc., 1540 Broadway, 24th Floor, New York, NY 10036, USA*

The ambition of atomic level (or atomic layer) processing (ALP) is to be able to control the deposition onto or etching away of atomic thicknesses of a target material selectively at a chosen substrate, and not at other substrates, through the choice of reagent and reactor conditions. In this talk we present a conceptual scheme for the ALP of metals [1] and a simulation approach to find which conditions to use for each type of deposition or etching.

In the general case, four types of process are conceivably in competition when a metal surface is treated with any reagent or reagent-combination: continuous deposition (CVD) or etching, or self-limiting pulsed deposition (ALD) or etching (ALE). We show that first principles thermodynamics based on density functional theory (DFT) of bulk and surfaces is a computationally-efficient approach for distinguishing between the four processes. Crossover temperatures and pressures can be estimated, with the accuracy depending on how entropy, coverage and diffusion are treated.

We use the example of ruthenium metal to illustrate the simulation strategy. Ru continues to be investigated as a possible seed layer for interconnect electroplating in the fabrication of electronic devices. Ru can also be used as a capacitor electrode and as a heterogeneous catalyst. Ru was one of the first noble metal ALD processes to be discovered [2] and, coincidentally, Ru oxidation was the subject of a pioneering exposition of DFT thermodynamics [3].

Ru metal or RuO_2 can be either deposited or etched depending on exposure to oxidants (O_2, O_3, O_2-plasma) or reductants (H_2 and a variety of Ru precursors) [4]. Quasi-catalytic cycling between metal and oxide is key to the deposition mechanism [5]. RuO_4 gas can play the role of deposition precursor or etch product, with the mechanism of etching recently computed by Shong *et al.* [6]. Low-temperature deposition allows substrate-selectivity, which can be enhanced by punctuating the process with an additional self-limiting etch step [7]. We therefore focus on the conditions for self-limiting versus continuous ALP of Ru metal, hydride, hydroxide and oxide with respect to H_2 and RuO_4 reagents.

References

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* *corresponding author e-mail: simon.elliott@schrodinger.com*