Chapter #5

Chemistry for CVD

1. WHAT DOES THE “C” STAND FOR ANYWAY?

The name says it all: Chemical Vapor deposition. CVD depends on the availability of a volatile chemical, which can be converted by some reaction into the desired solid film. We've already discussed how the vapors, once produced, can be transported to the substrate and heated up when they get there. Next we need to think about what makes the vapors in the first place (that is, volatility) and how these vapors can react in the gas phase or on the surfaces to be converted into the film.

We'd like to emphasize that in every CVD process, there is of necessity some reaction path that converts the vapors to a solid. Part of the task of designing the reactor and process is always to force this reaction to happen only where and when it is desired (typically on the substrate), and not everywhere else. Undesired reactions result in particles which can fall onto the substrates, coating of chamber walls, and clogging of exhaust openings. The approaches to achieving this selectivity typically rely on four levers: temperature, time, pressure, and surface specificity.

In a brief review we can't possibly hope to cover the vast field of how atoms interact with each other. The tutorial material is highly selective; we hope to at least provide enough familiarity with the most relevant terminology and concepts to help the reader negotiate the technical literature with confidence, and perhaps remind them of material they studied in school but haven't used since.
We'll start by recalling some of the basic concepts of how electrons and nuclei interact to produce atoms and bonds between them...

Although computational quantum chemistry has made tremendous strides in the last decade, most chemists still base much of their conceptual approach to understanding atoms on the classification of electronic states that arises from the only chemical system for which exact analytical solutions of the Schrodinger equation can be constructed: the hydrogen atom. In this simple case, the possible states for a single electron bound to a singly-charged positive nucleus can be described by three quantum numbers: \( n \), which gives the number of radial nodes of the wavefunction; \( l \), which specifies the total orbital angular momentum; and \( m \), which specified the angular momentum projected onto the z-axis.

1.1 Hydrogen and Its Friends: the Simplest View of Atomic Structure

In the one-electron atom, the energies of all the states of a given shell are the same (the states are "degenerate", a mathematical term with no implications about their moral fiber), with binding energy relative to a free electron state varying as the square of the ratio \( (Z/n) \), where \( Z \) is the nuclear charge (equation [5.1]).

\[
E = \frac{q^4 m e Z^2}{32 \pi^2 \varepsilon_0^2 h^2} \frac{1}{n^2}
\]

[5.1]

(Here \( q \) is the magnitude of the electron charge, \( m_e \) the electron mass, \( \varepsilon_0 \) the dielectric permittivity of free space, and \( h \) is Planck's constant divided by \( 2\pi \).) For \( Z=1, n=1 \), the binding energy is the ionization energy of hydrogen, about 13.6 eV. The "size" of the eigenfunctions is roughly the Bohr radius, 0.5 Angstrom, multiplied by \( (n^2/2Z) \). The wavefunctions for a given value of \( n \) are often known as "shells". The shells are often denoted by letters: K corresponds to \( n=1 \), L to \( n=2 \), M to \( n=3 \), etc.

As a consequence of the shrinkage and increase in binding energy with \( Z \), for more complex atoms with higher nuclear charge, the "inner" shells (small \( n \)) become very tiny and very strongly bound to the nucleus, and don't participate much in binding with other atoms. The outermost shells, with the highest values of \( n \), "see" only the shielded nuclear charge (the actual charge minus the charge from the inner electrons), and are thus much larger and more weakly bound. It is only these "valence" electrons that can participate...