**Context**

This report is a supporting document of the MATLAB program developed by Sam Borkent, based on the paper *“Numerical modelling of the plasma plume propagation and oxidation during pulsed laser deposition of complex oxide thin films”*, by Tom Wijnand, et al. (2020). The program was written to fulfil the requirements of a capita selecta of 5 EC, commissioned by Prof. Mark Huijben, of the Inorganic Materials Science (IMS) group of the University of Twente.

**Background**

Advances in modern technology are often driven by engineering materials with novel properties. One way to engineer the properties of a material is to reduce its dimensionality, as this constrains the propagation of waves and particles within the material to a certain preferential direction and alters its physical and statistical properties. For example, the dimensionality of a 3D bulk material can be reduced to a 2D thin film [?] or nanosheet [?], a 1D nanowire [?], or a 0D nanoparticle or quantum dot [?]. A well-studied and widely utilized technique to produce these low dimensional nanostructures is pulsed laser deposition (PLD). In PLD a high energy pulsed laser is focused on a target material in a vacuum chamber, the high energy density on the target surface causes the atoms in the target to ionize, resulting in the formation of an outward expanding plasma that propagates normal to the target surface. This plasma is then collected on a high temperature substrate surface, where it crystalizes into one of the aforementioned nanostructures. PLD enables epitaxial growth of a large variety of materials on a wide range of substrate materials. The most common materials that are being studied with PLD are complex metal oxides. This category of materials has been shown to exhibit exotic properties ranging from ferroelectricity [?] to superconductivity [?].

Another important specification of PLD is that is allows for stoichiometric transfer from target to substrate. This means that the composition of the target material is maintained during growth. To achieve this stoichiometric transfer a low pressure background gas is commonly introduced in the vacuum chamber. The primary functionality of this background gas is threefold. Firstly, if the kinetic energy of a particle arriving at the substrate surface is too high, it will undergo an elastic collision with the surface and bounce off. The background gas will result in additional collisions between particles and reduce the total kinetic energy of the plasma, so particles will stick to the substrate surface on arrival. Secondly, if oxygen gas is used, collisions with the background gas will result in oxidation of reactive species in the plasma, altering the oxidation state in which the plasma arrives at the substrate. Thirdly, the background gas reduces desorption of particles from the substrate, which can prevent oxygen depletion at the surface. In the case of oxygen gas, the background gas can also increase the oxidation of the substrate surface and potentially fill oxygen vacancies. These effects combined makes the choice of the background gas and background pressure some of the most important PLD growth parameters that can be tuned to produce the desired materials.

PLD can achieve high quality results quickly compared to other high-end methods, so increasing the scale of the technology is also being investigated. The aim is to produce homogeneous structures on large area wafers, so PLD can be applied for industrial chip and sensor fabrication. One major physical difference between large area and small scale PLD is that on a large wafer the entirety of the plasma plume is collected, while a small substrate only receives the centre of the plasma. The size of industrial wafers is much larger than the physical width of the expanding plasma, so in large area growth the plasma is scanned over the wafer surface to ensure even coverage. The composition and density can vary spatially within the plasma, so collecting the entire plasma instead of only the centre will affect the growth.

Modelling the propagation of the plasma particles and the interaction between the plasma and background gas could give insight into the spatial variation of the particle density and composition in the expanding plasma, which can be used to approximate the chemical composition and the kinetic energy of particles arriving at the substrate, which could be a helpful tool during target selection and PLD growth parameter optimization.

**Summary of Wijnand’s model**

Here the model created by Wijnand will be shortly summarized, for more in-depth information I refer the reader to the full paper. Wijnand’s model simulates the of PLD plasma particles originating from an TiO2 target propagation in an O2 background gas. As modelling every single particle (~1015 in total) individually is not possible with current computers, particles are collected together in computational bins with other particles of similar type, distance from target, velocity, and number of collisions. The particles in the background gas are modelled in a similar way, although the number of collisions is not tracked, and the background particles only consist of two velocity bins: one for zero velocity for stationary particles, and one for moving particles. The spatial expansion of the plasma plume is modelled by dividing space into a number of angular bins ranging from 0° (normal to target surface) to 90° (parallel to target surface.

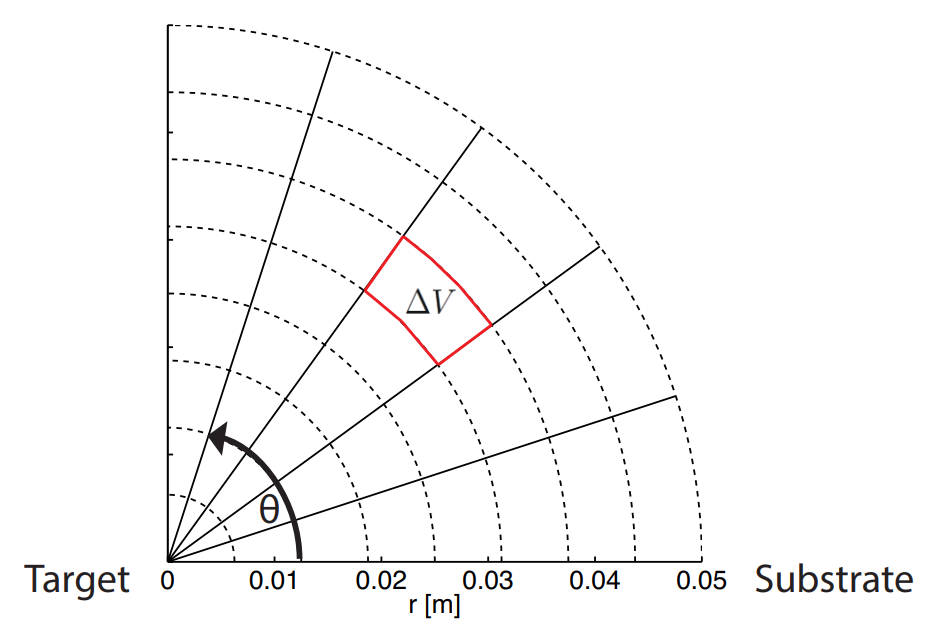


Figure - Schematic of the polar grid which represent the spatial computational bins of the numerical model.

**Types of collisions**

There are seven possible collisions between plasma and background gas species for a single metal oxide target with formula . For an oxide target with two metals and general formula there are twelve possible collisions: (1-3) for collisions between either one of the atoms in the plume and stationary background particles, (4-6) for the collisions of the plume atoms with high energy propagating background particles, (7) , (8) , (9) , for two identical particles within the plasma, (10) for collisions between the two metal atoms, and finally (11, 12) for collisions between the metal atoms and the oxygen atoms originating from the target. As result of an inelastic collision an oxidation reaction can occur, introducing new plume species with formulas , which increases the number of collision terms.

The initial velocity distribution separates identical particles in space, which means collisions between identical particles are relatively rare. When two identical particles with different velocities, traveling in the same direction, collide elastically, their velocities interchange. This results in a zero-net change in the plasma particle velocity distribution. Therefore, identical particle collisions are neglected.

If the two metal atoms are of similar mass (e.g. ), their initial average velocities will be close to each other. In this case the cross term is expected to be large. If the masses of the two metals vary greatly (e.g. ), their initial average velocities will be spaced apart, and consequently they will separate in space, resulting in a small collision term. However, if a significant amount of light metal atoms gets slowed down by the background gas, the heavy metal atom might still collide with the light metal, which would again increase the significance of the collision term.

**Collision probability**

* *Generalize for collisions with either background gas or other plasma species (plasma particle and collision medium)*

The paper by Wijnand considered the collision probability of a plasma particle colliding with a background gas particle to be:

Wijnand’s proposed collision probability within time interval is a function of the plasma particle velocity , and the background gas particle velocity . It is determined by the velocity of the plasma plume , the scattering cross-section , and the local density of particles of the background gas , with for the current radial bin, for the current angular bin, for the velocity bin of the background gas particle, and for the current time step. The scattering cross-section is determined as the sum of the cross-section of two colliding hard spheres with atomic radii. In the case of molecules, the hard sphere radius is assumed to be the sum of the atomic radii of its components, so in the case of O2 the cross-section will be , where is the atomic radius of oxygen. The local particle density of the background gas must be determined per velocity bin. As all background particles are initially assumed to be static, they all start out in the first velocity bin . Note that this expression is not a normalized probability, the factor gives the volume of the path traversed by a particle within one timestep, multiplying this by the density gives the number of particles within this volume. If the number of particles in this volume is greater than one, the collision probability is effectively 100%, as it is guaranteed there is at least one particle within its path.

There are some problems with this approach. Due to the high velocities of the plasma, multiple radial bins can be traversed within one time step, this makes it unclear which particle density to use in the expression. Also, the expression does not account for the relative difference in velocities between the plasma particle and the background particle. Logically, a plasma particle will never collide with a particle with the same or higher velocities, so if then . Also, one would assume there is a higher probability of colliding with a background particle with a lower relative velocity. It is important to include this if we want to accurately model collisions between different plasma species with similar velocities. A practical problem with calculating the number of particles that get scattered is the conservation of number of particles, as it must be ensured that no particles are destroyed or created.

To address these issues, a new approach was developed. There are two approaches to this. The first one is two calculate the collision probability for each traversed radial bin, based on the local background particle density, where only the fraction of particles that did not collide can traverse to the next radial bin. The second approach is to calculate the collision probability for the entire traversed path based on the average density and assume there is an equal probability of scattering within each bin. The first approach arguably closer resembles reality, although it increases the computational cost as one must include at least one additional loop over the traversed path. However, the use of the second approach can be justified by the quantized nature of the model, as one does not have any knowledge as to what happened between each time step, so assuming an equal fraction of collided particles gets scattered in each traversed bin is a fair assumption. A problem with the second approach is that if you do not know with which velocity and in which radial bin a collision happens then you cannot accurately update the number of particles. How we tackle this problem is with the assumption that a plasma particle will collide with the lowest velocities first. Only when all the particles in the lowest velocity bin have been scattered, the plasma particle will collide with the background particles within the next lowest velocity bin.

Let us continue with the second approach which will be formulated mathematically. The number of radial bins traversed by a particle moving with velocity within one time step is given by:

The average density of these traversed bins is:

The collisions probability is written slightly different:

Which we extend with a factor that accounts for the relative difference between the plasma and background particle velocities:

So, now if no collision takes place, and collision is more likely between particles with a large difference in velocity.

Wijnand’s model assumes that each particle can only undergo one collision each timestep, no matter how large the time step. This assumption is only holds if the spatial and temporal resolutions are small enough that the collision rate is always smaller than one.