Large-Scale Molecular Dynamics Simulations of Plasma Sputter Deposition.
Pascal Brault¹, Guy Moebi²

¹Groupe de Recherches sur l'Energetique des Milieux Ionises, UMR6606 CNRS
ESPEO Université d'Orléans BP6744, F-45067 ORLEANS Cedex 2
²Centre de Ressources Informatiques de Haute-Normandie
Parc d'Activités Technologiques de la Vatine, 76130 Mont St-Aignan

Abstract:
We describe thin film growth mimicking sputter deposition using Molecular Dynamics simulations. Pd was deposited on graphite surfaces and is shown to form clusters. Increasing kinetic energy and surface disorder leads to different film morphologies.

1. Introduction

Atomic simulations of complex systems as those relevant in plasma deposition become possible due to the recent development of large scale computing facilities especially parallel supercomputer.

Recent experiments on sputter deposition of palladium have shown that new growth modes compared to vacuum deposition are possible due to the simultaneous exposure of the substrate (a-C or C(0001)) to sputtered metal atoms (Pd) and plasma ions (Ar⁺). Especially, a transition between cluster growth and low thickness (<80 Å) continuous film occurs for a special combination of the ratio of ion flux to metal atom flux and the impinging metal kinetic energy [1, 2].

For deeper insight of processes responsible for the transition from cluster growth to continuous film growth, Molecular Dynamics calculations using tight binding many body potential in the second moment approximation [3] are carried out for describing the Pd-Pd interactions when adsorbed on the graphite surfaces. Effects of both kinetic energy of incoming Pd atoms and surface disorder on growth are examined.

2. Parallel Molecular Dynamics

Molecular Dynamics (MD) is a simulation technique in which classical equations are solved for a set of atoms or molecules. This leads to the well-known classical Newton set of equations describing the motion of atoms. This can be written in the form, for particle interactions with surface atoms:
\[
\dot{x}_i = \frac{f_{x_i}}{m_i} = -\frac{1}{m_i} \left( \frac{\partial}{\partial x_i} V_s + \sum_{j \neq i} \frac{\partial}{\partial x_j} V_{ij} \right)
\]
\[
\dot{y}_i = \frac{f_{y_i}}{m_i} = -\frac{1}{m_i} \left( \frac{\partial}{\partial y_i} V_s + \sum_{j \neq i} \frac{\partial}{\partial y_j} V_{ij} \right)
\]
\[
\dot{z}_i = \frac{f_{z_i}}{m_i} = -\frac{1}{m_i} \left( \frac{\partial}{\partial z_i} V_s + \sum_{j \neq i} \frac{\partial}{\partial z_j} V_{ij} \right)
\]

where \( m_i \) is the mass of the \( i \)th incoming atom interacting through the potential \( V \) with surface atoms and among other adsorbed atoms through the potential \( V_{ij} \). In principle we should have the same set of equations for the surface atoms: they interact among themselves and also with adsorbed atoms. In the following the surface atoms are at their fixed positions. Disordered surface is obtained by randomly displacing them. This is a coarse approximation that can be intended only for qualitative reasoning. In such a way it is necessary to use a trick for dissipating energy through the solid for allowing bonding to the surface. As a first attempt, we make use of quenched molecular dynamics: if \( \dot{F} < 0 \) at each time step, then the velocity of the atom is reset to a velocity randomly chosen in Maxwell distribution at surface temperature which is fixed here to \( T_s = 300 \) K.

Simulating deposition need to release atoms one after each other with a time delay \( \Delta t \) reasonable when comparing to experiments, i.e. either the flux reproduce exactly the ones encountered in experiments or this time delay is sufficient for allowing thermal relaxation of the already deposited atoms and/or thermal relaxation of surface atoms (when they are allowed to move). In our case we choose the latter one, which allow to reduce computer time thus \( \Delta t \) was fixed to 2ps.

Implementing suitable interatomic potentials is certainly the most important issue in molecular dynamics calculations. For describing transition metals like palladium, we use tight binding potential in the second moment approximation (TB-SMA) [3]. Such a potential is non pairwise in the sense that if atom \( i \) interact with atom \( j \), the atoms surrounding atom \( j \) are explicitly taken into account as it can be shown in the following TB-SMA force equation:

\[
\vec{F}_i = \sum_{j \neq i, r_{ij} < r_c} \left\{ 2A \xi q \exp\left(-p\frac{r_{ij}}{r_0} - 1\right) - \frac{\xi q}{r_0} \left[ \frac{1}{\sqrt{E_i^b}} + \frac{1}{\sqrt{r_{ij}^b}} \right] \exp\left(-2q\frac{r_{ij}}{r_0} - 1\right) \right\} \frac{\vec{r}_{ij}}{r_{ij}}
\]

with

\[
E_i^b = \sum_{j \neq i} \exp\left(-2q\frac{r_{ij}}{r_0} - 1\right) \quad \text{et} \quad E_{ij}^b = \sum_{k \neq j} \exp\left(-2q\frac{r_{jk}}{r_0} - 1\right)
\]

where \( r_0 \) is the first neighbor distance. For palladium it is 2.75 Å. The interaction is cut off at \( r_c^{TB} = 2.5r_0 \). \( r_{ij} \) is the interatomic distance between \( i \) and \( j \) atom. \( A, \alpha, q, \xi \) are the TB-SMA parameters [3]. Even if this potential has two-body form, it is needed for each \( j \) atom to search for all neighbors within the cutoff radius \( r_c^{TB} \) and to calculate the sum \( E_{ij}^b \). This makes the calculations computer time consuming, especially when \( r_c^{TB} \) becomes quite large. While \( r_c^{TB} \) can be restricted to \( r_0 \) in bulk materials (because atoms remains at their equilibrium position), when deposition simulations are undergone, it is necessary to use larger cutoff radii, especially for accounting interactions with diffusing atoms. The value we choose is the
smallest which do not change the results. It allows taking into account 92 neighbors (for palladium), each neighbor interacting with its own 92 neighbors (when comparing to bulk materials). For ultrathin films, the number of neighbors is reduced. But it is clear that high performance computers are required for treating necessary long time deposition with such kind of interactions.

For interactions with fixed C atoms, we used a Lennard Jones potential:

\[ V_{\text{Pd-C}}(r) = 4\varepsilon_{\text{Pd-C}} \left( \left( \frac{\sigma_{\text{Pd-C}}}{r} \right)^{12} - \left( \frac{\sigma_{\text{Pd-C}}}{r} \right)^{6} \right) \]

The Pd-C Lennard-Jones interaction potential is obtained by using the Lorentz-Berthelot mixing rule [4]:

\[ \varepsilon_{\text{Pd-C}} = (\varepsilon_{\text{Pd}}\varepsilon_{\text{C}})^{\frac{1}{2}} \quad \text{and} \quad \sigma_{\text{Pd-C}} = \frac{\sigma_{\text{Pd}} + \sigma_{\text{C}}}{2} \]

with \( \varepsilon_{\text{Pd}} = 0.426 \text{ eV} \) and \( \sigma_{\text{Pd}} = 2.52 \text{ Å} \) [5]. The parameters for C-C interactions can be found in reference [6] and the values are: \( \varepsilon_{\text{C}} = 2.414 \times 10^{-3} \text{ eV} \) and \( \sigma_{\text{C}} = 3.40 \text{ Å} \). This gives: \( \varepsilon_{\text{Pd-C}} = 0.0327 \text{ eV} \) and \( \sigma_{\text{Pd-C}} = 2.99 \).

The equations of motion are solved using the Verlet velocity algorithm [7,8]. A link-cell list is used to speed-up the computations. Due to the non-pairwise interactions, the CPU time is not reduced to \( O(N) \), where \( N \) is the number of particle. The time interval required for calculating the forces is \( dt = 1 \text{ fs} \).

For parallel implementation, we used the atom-decomposition scheme also known as replicated data method [9]. This method is used because the filling of space is expected not to be complete so spatial-decomposition scheme can not be an efficient scheme [9]. The parallel instruction library OpenMP has been found to be more efficient than message passing libraries as MPI because the calculations are performed on a shared memory supercomputer (Origin 2000, 64 nodes, CRIHAN, France). Briefly, N/p particles are treated by each p nodes during all the course of the simulation. At the same time, all information about each particle is known from each p nodes.

3. Results and discussions

A set of simulations of Pd deposition was performed onto crystalline C(0001) surface. The simulation cell is 3 atomic layers of 103Åx102Å leading to a rigid substrate of 12369 C atoms. One monolayer (ML) corresponds to 1521 atoms for a Pd fcc (111) structure. Three kinds of surfaces have been built: an atomically smooth (C1), and a highly roughened surface where atoms are randomly displaced by 50% of the C-C distance, \( \sigma_{\text{C-C}} = 1.42 \text{ Å} \) (C3). Each palladium atom are launched every 2 ps. All the Pd atoms interact simultaneously with other palladium atoms in the cutoff radius \( r_0 \) and with C rigid substrate atoms with a cutoff radius \( r_c = 2.5\sigma_{\text{Pd-C}} \). The calculations have been performed at 0.31 ML (500 Pd atoms), 0.62 ML (1000 Pd atoms) and 0.93 ML (1500 Pd atoms). The Pd initial kinetic energies are 0.026 and 1. eV. In the former case, it simulates a gas at \( T_g = 300 \text{ K} \). This occurs when sputtered Pd atoms travels across a buffer gas at sufficient pressure. In the latter case either the energy \( E_g = 1\text{eV} \) is directed towards the surface as for a beam, or simulate a vapor-like at temperature \( T_v = 1\text{eV} \). This occurs for sputtering experiments at low pressure where a small amount of buffered gas randomizes sputtered atoms velocity. The following Table 1 summarizes the statistics of deposition and a typical set of snapshots is displayed in Fig. 1. While corrugating the surface do not modify evidently the statistics of the clusters, increasing energy changes size and number of clusters. Depending on the way of generating the Pd atoms (i. e. beam or vapor) influences the morphology of the clusters. Beam simulation at 1 eV gives an initially
large cluster number, which quickly decrease to value smaller than for thermalized depositing atom growth. At the same the cluster size is smaller at low coverage and is larger at higher coverage. In 1 eV vapor–like simulation, at low coverage larger clusters are growing but with a smaller density (always when comparing with 0.03 eV deposition). At

<table>
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<th>$T_g = 0.03$ eV</th>
<th>$N_{pd}$</th>
<th>$C_x$</th>
<th>$Z_c$ (%)</th>
<th>$N_{cl}$</th>
<th>$&lt;a&gt;$ (a.u.)</th>
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<tr>
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<td>61</td>
<td>504</td>
<td></td>
</tr>
<tr>
<td>1000(b)</td>
<td>C3</td>
<td>20</td>
<td>70</td>
<td>439</td>
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<tr>
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<td>32</td>
<td>47</td>
<td>1027</td>
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<td>56</td>
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<td>43</td>
<td>37</td>
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<td>20</td>
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<tr>
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<td>35</td>
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<tr>
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<tr>
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<td>C3</td>
<td>46</td>
<td>26</td>
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Table 1. Statistics of the deposited clusters: $N_{pd}$ is the number of deposited atoms; $C_x$ is the kind of disordered surface; $Z_c$ is the area covered by the clusters; $N_{cl}$ is the cluster number, $<a>$ is the mean cluster area. (x) x = a–f refers to the labels of Fig. 1.

Fig 1. Snapshots of deposition Pd deposition on graphite for $T_g = 0.026$ eV with $\theta = 0.31$ ML (a), $\theta = 0.62$ ML (b), $\theta = 0.93$ ML (c) and $T_g = 1.0$ eV with $\theta = 0.31$ ML (d), $\theta = 0.62$ ML (e), $\theta = 0.93$ ML (f).
higher coverage, the density remains always lower and cluster larger and do not leads to an inversion in statistics as for beams where starting with very small clusters nevertheless leads to large cluster at the expense of a dramatic decrease of density. In all cases, for the same amount of deposited atoms, the fraction of covered surface remains the same in all situations.

4. Conclusion

Atomic simulations of deposition using realistic potential are able to describe dynamical processes during growth. In the present study, the effect of how kinetic energy is provided to depositing atoms is examined. Directed energy as for beam deposition or random energy as for vapor like deposition lead to different initial cluster densities. The evolution is always towards very large clusters compared to thermalized depositing atom deposition.

References.