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Molecular dynamics simulations of supported metal nanocatalyst formation by plasma sputtering

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ABSTRACT

Magnetron sputtering is a widely used physical vapor deposition technique for deposition and formation of nanocatalyst thin films and clusters. Nevertheless, so far only few studies investigated this formation process at the fundamental level. We here review atomic scale molecular dynamics simulations aimed at elucidating the nanocatalyst growth process through magnetron sputtering. We first introduce the basic magnetron sputtering background and machinery of molecular dynamics simulations, and then describe the studies conducted in this field so far. We also present a perspective view on how the field may be developed further.

1. Introduction

Magnetron plasma sputter deposition is a well-established deposition technique that is widely used in research and industry [1]. It can be used as an atom or cluster source [2,3] for which composition, kinetic energies and angle distributions (more or less peaked) are well defined. Due to the atomic nature of the plasma sputtering process, deposition of thin films in the form of supported clusters of well-defined composition, structure and morphology has become possible. This is highly important in catalysis, where fabrication processes that precisely meet such requirements are highly demanded [4]. Heterogeneous catalysis is typically concerned with supported assemblies of nano-sized particles, dispersed on a support with a large surface area [5,6]. Due to the complexity of the catalyst formation process, predictions of the size, morphology and atomic structure of the supported catalyst clusters is a very challenging task. Computer simulations may therefore prove to be very useful in delivering precisely such data.

Molecular dynamics (MD) is a computer simulation technique in which the system evolution is followed at the atomic level and hence, MD is well suited to describe materials at the atomic scale [7–12]. Since magnetron sputter deposition is an atomic process, MD simulations are the tool par excellence to investigate the involved growth process [13–20]. However, until now, MD simulations have not often been applied for investigating catalyst synthesis in general and catalyst synthesis by magnetron sputtering and other physical vapor deposition processes in specific, in part due to the complexity of the process. Such simulations, on the other hand, have often been used for the determination of equilibrium structures, and the study and effects of catalytic reactions, also in the context of a plasma environment [21,22].

In this contribution we will therefore focus on the capabilities of MD for predicting the growth of nanocatalysts by magnetron sputtering. First, we will describe the input parameters of MD simulations and pay specific attention to crucial issues such as energy distributions and transfer of high energy particles (0.1–10 s eV). Subsequently, we will elaborate on the growth of platinum nanocatalyst particles based on MD simulations. We will also provide a perspective on how the field may be developed further. Finally a conclusion will be given.

2. Molecular dynamics simulations for magnetron sputtering

We first briefly recall the main features of magnetron sputtering as an atom or cluster source. Basically, a plasma of the buffer gas (typically argon) is created by a direct current or a radiofrequency power supply applied to an electrode located inside a vacuum chamber. The pressure is typically in the range 0.01–100 Pa. As the electrode is usually negatively biased (usually in the range from 100 to 1000 V), positive ions of the buffer gas are bombarding the electrode, now called the target, containing the catalyst material.

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Since typical sputtering thresholds are around 20 eV, such ion bombardment results in the ejection of atoms from the target. These sputtered atoms will travel from the target through the plasma to the substrate and eventually deposit on the substrate surface. During the transport of the sputtered material through the plasma, the energy distribution of the sputtered atoms will change due to collisions with the buffer gas atoms, which in turn depends on the buffer gas pressure. If the pressure is sufficiently high, the sputtered atoms show a relatively high self-collision probability and start to form clusters in the plasma phase. This phenomenon is called gas condensation and is the basis of the design of nanocluster beam sources [3]. The energy distribution function of the sputtered atoms leaving the target can be approximated by the so-called Thomson formula [23–25]:

$$f(E) \propto \frac{1-\left(\frac{E_{coh}+E}{\gamma E_{\mathrm{Ar}^+}}\right)^{1/2}}{E^2\left(1+\frac{E_{coh}}{E}\right)^3} \tag{1}$$

where E_{coh} is the cohesive energy of the target material, E is the energy of the ejected atoms, γ is the kinetic energy mass transfer factor, and E_{Ar^+} is the kinetic energy of the impinging Ar-ions.

The final energy E_F after n collisions along the path from target to substrate of a sputtered atom with energy E when leaving the target is given by [25]:

$$E_F = (E - k_B T_g)\exp\left\lfloor n\ln\left(\frac{E_f}{E_i}\right)\right\rfloor + k_B T_g$$

here, $E_f/E_i = 1 - \gamma/2$ is the ratio of energies after and before a collision [26]. The kinetic energy mass transfer factor is defined as:

$$\gamma = 4\frac{m_g m_s}{(m_g + m_s)^2}$$

where m_g and m_s are gas/plasma phase atom (e.g. argon) and sputtered atom masses, respectively. The number of collisions that take place in the gas is given by:

$$n = \frac{dP\tau}{kBT_g}$$

where T_g is the sputtering gas temperature, d is the traveled distance, P is the sputtering gas pressure, and τ is the collision cross section assuming hard-core interactions. In order to calculate the energy loss (E_F) of sputtered atoms with the gas atoms, a Maxwell–Boltzmann (MB) distribution at T_g is assumed for the gas. In most sputter deposition sources this corresponds to $T_g = 300$ K and $E_g = kBT_g$. Because we search for the complete energy distribution of sputtered atoms, for each E_g in the Maxwell–Boltzmann energy distribution for the gas, the energy loss is calculated for a fixed value of the kinetic energy E of a sputtered atom. This is repeated for each E in the Thompson distribution and weighted by the collision probability, which is simply the convolution of $f(E)$ and the MB distribution at T_g [25]. Initial velocities or equivalently kinetic energies can be readily obtained from such a distribution. The velocities of the sputtered atoms can also be sampled from a Maxwell–Gaussian distribution with a mean kinetic energy corresponding to the energy loss calculated from Eq. (1) with randomly selected incident angles. In Fig. 1, we show a typical energy distribution for Pt sputtered at various Ar pressures P for a given target-to-substrate distance and impinging Ar$^+$ ion energy on the target.

MD simulations make use of this information by randomly selecting initial velocities from such distribution functions, while the initial positions of atoms arriving at the substrate are typically randomly chosen in $\{x,y\}$-directions and chosen to be beyond the interaction range of the interaction potential used in the z-direction.

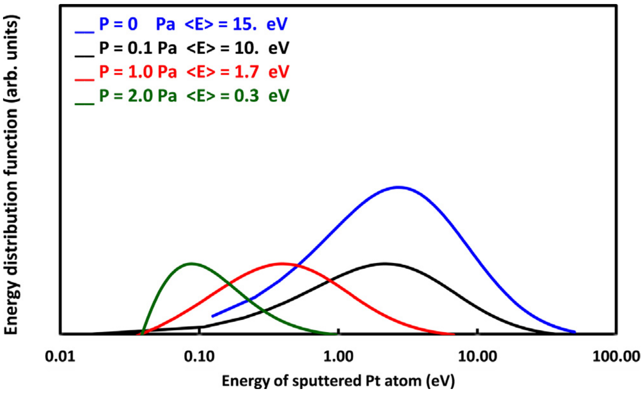

Fig. 1. Example of energy distribution functions of Pt atoms arriving at the substrate located at 10 cm from the sputtered target biased at 300 V. Plots are given for different Ar pressures P (log scale for the abscissae).

In practice, MD simulations of the sputter deposition process require integrating the Newton equations of motion for the assembly of incoming atoms (or molecules or clusters) as well as the substrate atoms. As the substrate atoms' trajectories are also explicitly followed through space and time, the response of the substrate to individual atom impacts can be monitored as well.

The Newton equation of motion reads:

$$\frac{\partial^2 \rightarrow r_i(t)}{\partial t^2} = \frac{1}{m_i}\vec{f}_i, \text{ with the force}$$

$$\vec{f}_i = -\frac{\partial}{\partial \rightarrow r}V(\rightarrow r_1(t), \rightarrow r_2(t), \ldots, \rightarrow r_N(t)) \tag{2}$$

where $\vec{r}_i(t)$ is the instantaneous position of atom i with mass m_i at time t, and V is the potential energy function governing all interatomic interactions.

Solving this equation thus requires the availability of a suitable interatomic interaction potential V. For metal catalysts many-body potentials are required and constructing suitable potentials (especially for accurately describing the metal–support interactions), is an active field of research [27–29]. As we will describe in the perspective section, we believe this is an important field of development for advancing theoretical studies of plasma sputter deposition.

A class of potentials often used for describing catalyst evolution under various conditions is the Embedded Atom Model (EAM) [30–33]. The EAM potential is based on a concept borrowed from density functional theory stipulating that in general the energy of a solid is a unique functional of the electron density. The embedded-atom method uses the concept of electron (charge) density to describe metallic bonding. Essentially, each atom contributes through a spherical, exponentially decaying field of electron charge, centered at its nucleus, to the overall charge density of the system. Binding of atoms is modeled as embedding these atoms in this "pool" of charge, where the energy gained by embedding an atom at location r is some function of the local density. Various collections of EAM parameters of metals of interest for catalysis, and for their alloys have been developed by Zhou et al. [32] and Lin et al. [33].

The EAM potential energy E_{pot} of the system can be expressed as:

$$E_{pot} = \sum_{i=1}^{N} E_i = \frac{1}{2}\sum_{i=1}^{N}\sum_{i,j,i\neq j}^{N}\phi_{ij}(r_{ij}) + \sum_{i=1}^{N}F_i(\rho_i) \tag{3}$$