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Review

Modeling the Deposition of Thin Films of Transition Metal Nitrides

Alexander Goncharov [1,2,*], Andrii Yunda [3], Ivan Kolinko [2,*], Grygoriy Kornich [4,5] and Dmytro Shyrokorad [4]

1 Institute of Materials Science, Slovak University of Technology in Bratislava, Jána Bottu 25, 917 24 Trnava, Slovakia
2 Department of Complex Systems Modeling, Sumy State University, 40007 Sumy, Ukraine
3 Institute of Applied Physics, National Academy of Sciences of Ukraine, 40000 Sumy, Ukraine; anyu35@gmail.com
4 Computer Sciences and Technologies Faculty, National University Zaporizhzhia Polytechnic, 64, Zhukovskogo Str., 69063 Zaporizhzhia, Ukraine; gvkornich@gmail.com (G.K.); hoveringphoenix@gmail.com (D.S.)
5 Faculty of Physics and Astronomy (EP3), Universität Würzburg, D-97074 Würzburg, Germany
* Correspondence: o.goncharov@mss.sumdu.edu.ua (A.G.); ivankolinko@ukr.net (I.K.)

Abstract: This paper presents an overview of studies dedicated to the atomic-discrete modeling of the growth process of film coatings that comprise mononitrides of transition and post-transition metals. The main modeling approaches are the Monte Carlo and molecular dynamics methods as well as their combinations with analytical contributions. The molecular dynamics method is more accurate compared to the Monte Carlo method but has disadvantages related to the time scale. Given this, the adoption of accelerated molecular dynamics methods is viewed as a promising approach for directly simulating the specified processes. These methods can be implemented just after the relaxation of the collision stage in the area of the deposited particle between the deposition events to simulate the realistic density of the incident beam and accompanied long-term mass transfer processes.

Keywords: nitrides; thin films; Monte Carlo; molecular dynamics

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1. Introduction

One of the features of modern technologies is the application of nanoscale coatings to improve the physical, mechanical, chemical, and tribological properties of the surfaces of many materials that are widely used in electronics, space technology, mechanical engineering, metallurgy, and other fields [1].

There are a wide variety of methods for the fabrication of film coatings, including physical vapor deposition (PVD), chemical vapor deposition (CVD), electronic precipitation/electronic coating, sol–gel technique, rotating coating, spray coating, electrodeposition, and self-assembling [2]. PVD techniques involve the transfer of materials on an atomic level under vacuum conditions. Among the advantages of PVD, the following can be highlighted: superior properties compared to the underlying substrate, applicability for a wide range of inorganic and organic materials, and eco-friendliness [3]. The most popular PVD techniques are magnetron and ion-plasma sputtering, which will be considered as the modeling subject of this discussion. General patterns of microstructure formation affect all functional coatings from metals and their simple compounds (oxides, carbides, nitrides, borides, etc.) to high-entropy solid solutions. It has been experimentally demonstrated that physical and mechanical properties, such as microhardness, strength, and plasticity of the deposits, are precisely determined by the features of their structure [4,5].

The formation of the coating structure type primarily depends on the homologous temperature T/T_m, defined as the ratio of the thermodynamic temperature of the deposited coating material and its melting point [6–8]. The homologous temperature determines

the thermally induced mobility of the adatoms on the surface of the growing nanocrystalline coating.

The presence of other factors influencing the structure formation of the coating depends on the method of its attainment. For example, during magnetron sputtering, the average energy of the bombarding ions (determined by the bias potential applied to the substrate) and the ratio of flows of ions and neutral atoms are added to the homologous temperature [9–11]. In general, the process of obtaining structured film coatings with predefined physical and mechanical properties depends on many parameters. Therefore, determining the physical properties of coatings "a priori" is a complex problem. Mathematical modeling of the physical processes of coating formation provides significant support in this regard.

Mononitrides of transition metals are the most attractive objects for modeling. Firstly, they are the most popular compounds used as functional coatings due to their high hardness and melting point. Secondly, they have a simple cubic syngony and two possible growth directions <111> and <200> [4,12]. Moreover, depending on the sputtering parameters, it is possible to switch from one growth direction to another (Figures 1 and 2).

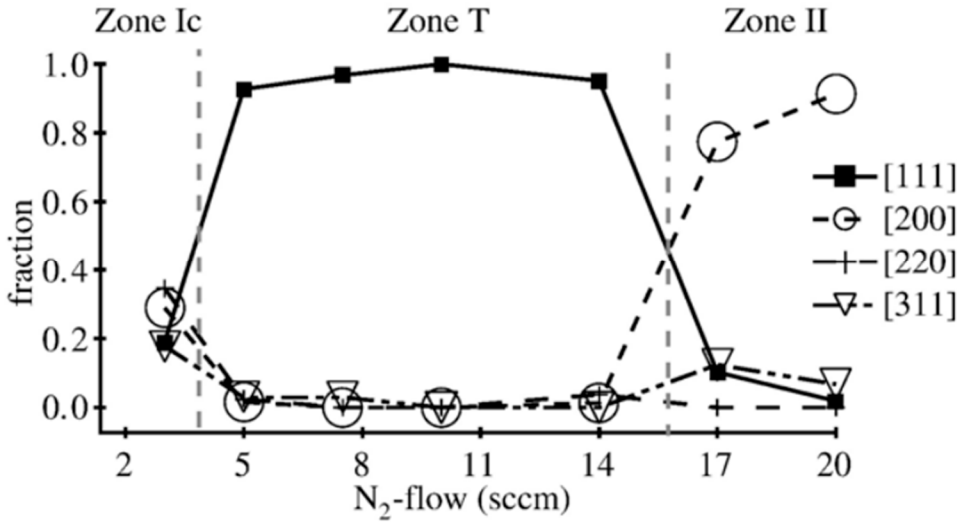

Figure 1. The volume fraction of grains of a specific orientation as a function of the reactive gas flow during TiN sputtering. The transition from a random orientation to [111] and finally to [200] is clearly visible [13].

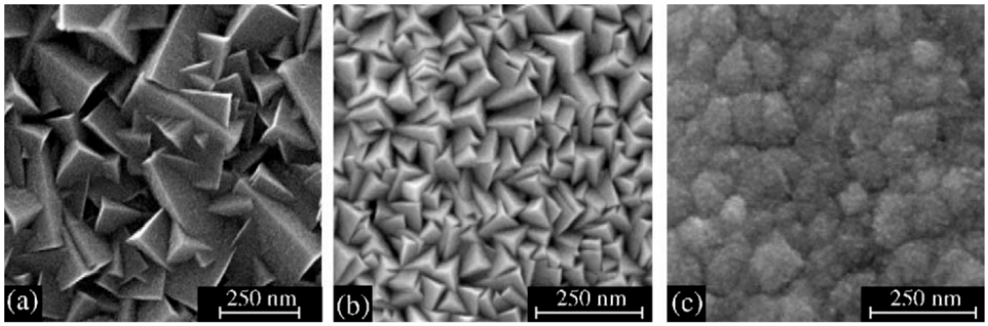

Figure 2. SEM images of the topography of TiN films obtained by reactive sputtering at (**a**) 3, (**b**) 5, and (**c**) 20 sccm [13]. This figure corresponds to the diagram of the predominant orientations shown in Figure 1.

In this work, the main atomic-discrete methods of mathematical modeling of the structure growth of nanoscale coatings are discussed using the example of transition metal mononitrides.

2. Methods for Modeling Multiatomic Systems

Today, there are many methods for modeling multiatomic systems. They are distinguished by different degrees of determinism, starting from the pure stochastic Monte Carlo (MC) method, and ending with the fully deterministic method of molecular dynamics (MD) (Figure 3) [14]. In the MD method [14,15], atomic positions are obtained by numerical solution of the differential motion equations of atoms. These positions, when joined over time, depict the real-time dynamics of individual atoms. In stochastic methods, the positions of the atoms are not related in time. For example, in an MC simulation, positions are stochastically generated, with the atomic configuration depending only on the previous configuration. In other simulation methods, positions are calculated from hybrid schemes that incorporate both stochastic characteristics, as in MC, and some deterministic characteristics, as in an MD approach.

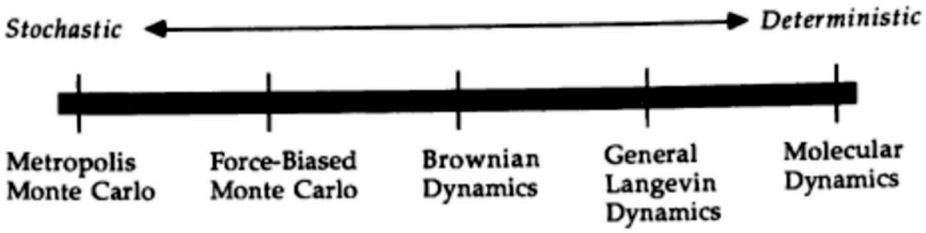

Figure 3. The relative degree of determinism in various methods of atomic-discrete modeling [14].

In the Monte Carlo method, the processes or events occurring on the deposition surface, namely, various diffusion processes, adsorption and desorption processes, and others (Figure 4), are considered random like Brownian motion. Accordingly, the probabilities of occurrence of each event for a single particle or atom at a given time are considered (calculated), and the event with the highest probability of occurrence is selected.

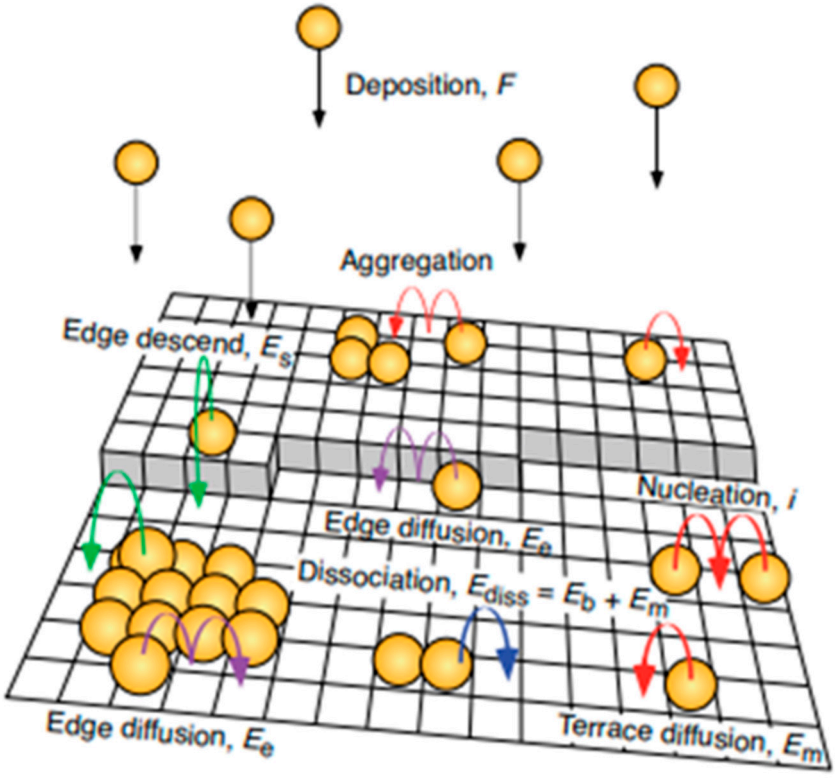

Figure 4. Illustration of the various diffusion processes [16].

The widespread popularity of MD methods, particularly in recent decades, is due to the development of many-body potentials [17–22] and a significant increase in the computational power, which, within the general simplicity of the basic algorithm (Figure 5), allows for modeling large-scale atomic systems over a relatively long time [23].

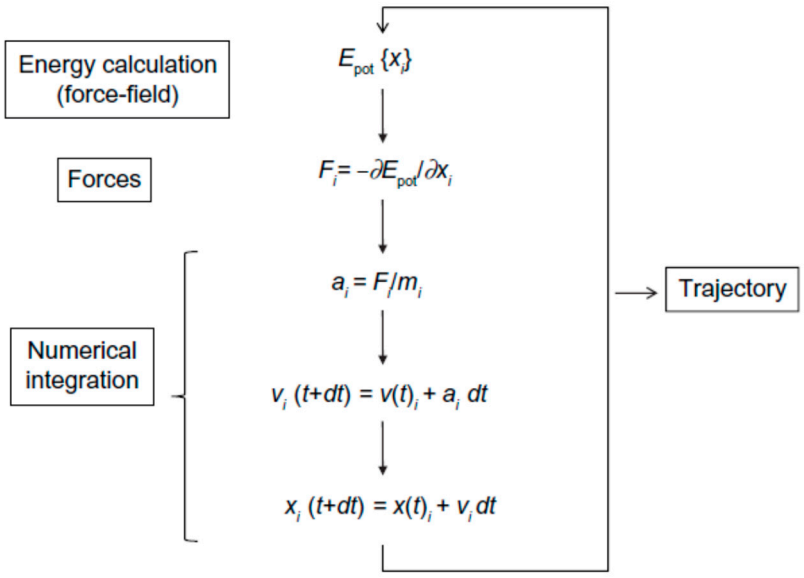

Figure 5. Basic MD algorithm. Abbreviations: E_{pot}—potential energy; t—simulation time; dt—time step; for each spatial coordinate of N simulated atoms (i): x is the coordinate of the atom; F is the force component; a is acceleration; m is the mass of an atom; v is speed [23].

MD methods are a powerful tool for simulating thin film growth. They take into account a wide range of physical and chemical properties of materials and allow for realistic results that are consistent with experiments. Molecular dynamics involves the use of different interaction potentials. At moderate to high interaction energies, typically exceeding 100 eV, the potentials governing atomic collision processes can be adequately described using pair potentials. These pair potentials model the screened Coulomb interaction between atomic nuclei. However, when it comes to interatomic interactions in metallic solids at or near thermal equilibrium, using additive pair potentials provides only a limited description. To address this limitation, many-body interaction potentials have been developed, offering a significantly improved description of both bulk and surface properties in metallic materials. These properties encompass surface relaxation and reconstruction, phonon dispersion relations (including surface phonons), bulk defect structure and energy, fracture behavior, and various other characteristics [24].

A significant limitation of this approach is the picosecond (sometimes nanosecond) interval of the available simulation time, which has a fundamental nature and is associated with femtosecond steps in the numerical integration of the motion equations of atoms. Compared to the classical MD approach, using accelerated MD methods [25,26] appears to be promising for the direct simulation of the atomic deposition process. Assuming that the selection of parameters and modeling conditions is felicitous, these methods allow for extending the available simulation time by several orders of magnitude in the case of an atomic system, where so-called rare (in many cases thermally activated) movements of atoms are occurring. These methods, including temperature-accelerated dynamics [27–29], hyperdynamics [30,31], and the method of parallel replicas [32,33], are still in the process of being improved (for example, [34–36]), but already have significant practical applications [26,37–40].

In [40], a bond-boost approach to accelerate molecular dynamics was proposed and its application to kinetic phenomena associated with thin film growth was demonstrated. Research into the diffusion of Cu atoms on Cu(001), Al adatoms on the Al(110) surface,

and Co clusters on Cu(001) was presented to illustrate different aspects of the method. For this purpose, the bond-reinforcement method was extended to perform accelerated initial condition simulation (AIMD).

In papers [41,42], simulations of the diffusion of vacancies in the crystal were carried out using various methods of accelerated MD and their versions. Comparisons were provided between these methods and classical MD methods. The obtained results showed wide possibilities for adequate modifications of accelerated methods and the evidence of their application for the systems with rare events occurring over long time intervals, particularly for the atomic deposition of thin films on substrates.

A possible approach to model deposition processes is to divide the process into two stages: direct deposition of an atom on the crystal surface (using classical MD) and diffusion of the atom on the surface (using accelerated MD) [26]. This makes it possible to achieve comparable deposition rates of the computer simulation and the experiment.

2.1. Monte Carlo Simulation

Simulations by the MC and kinetic monte carlo (KMC) methods are successfully used to predict the morphology of thin film growth at time and space intervals sufficient to study the technological process [43–47]. They can reproduce the random nature of the growth process and make it possible to use various atomic processes, whose rates are measured by more accurate models such as the MD method or first-principles methods such as density functional theory (DFT). During the last few decades, several MC models based on two-dimensional (2D) or three-dimensional (3D) rigid lattices were proposed in the literature [46]. The MC/KMC methods are successfully applied to different categories of deposition processes: PVD, CVD, ALD, and electrodeposition [48].

It is necessary to consider both metal and nitrogen atoms in the elementary events of deposition and diffusion during the simulation process. Thus, in [49], a significant difference in the migration rates of metal and nitrogen atoms, as well as the influence of TiN_2 trimers on the transport properties of the surface was confirmed by the MD simulation of the growth of the TiN surface (001).

In [46], a three-dimensional KMC model was developed. This computational tool was employed to replicate the microstructure and growth patterns of thin films of cubic transition metal nitrides (TMNs) formed through reactive magnetron sputtering. The findings showcased here pertain specifically to stoichiometric TiN, serving as a representative example of TMN. The model is constructed upon a stable NaCl-type lattice and encompasses the processes of nitrogen and titanium atom deposition as well as diffusion. The simulation was performed with a uniform flow of normally falling incoming particles. The ballistic deposition model is parameterized by r_0, which represents the capture distance at which particles can adhere to the surface. Two diffusion models based on different methods of calculating the activation energy for atomic jumps were used. The influence of temperature (300–500 K), deposition flow (0.1–100 monolayers/s), and parameter r_0 (1.5–6.0 Å) on growth morphology was presented. Microstructures that range from highly porous straight pillars with [001] orientation and a smooth top surface to pillars with different crystallographic facets formed by kinetic constraints, energy, and shadowing effects were reproduced. The emergence of facets is a direct result of the diffusion model, incorporating intrinsic (minimizing energy) diffusion anisotropy, although, at this point, we did not explicitly account for crystallographic diffusion anisotropy. We conducted a quantitative analysis of the time-dependent changes in morphology to ascertain the growth indicators β and α for roughness. The values $\alpha \approx 0.7$ and $\beta = 0.24$ obtained for TiN films correlate with existing experimental data. The KMC model can be further extended to reproduce more complex mechanisms. For example, to simulate anisotropic surface diffusion and grain boundary migration. These mechanisms are the basis of the competitive columnar growth and are observed in TiN-based polycrystalline films.

Further development of the model was carried out in [50] (Figure 6). The growth of TiN columnar thin films was simulated under the conditions of the geometry of inclination

at an angle with the help of atomistic calculations by the KMC method using the MODENA code. The influence of the substrate temperature (300, 400, and 500 K) on the morphology of the layers (inclination angle of the columns, average density of the layer, compactness, surface roughness) was studied by changing the angle of inclination of the substrate α from 5° to 85°. In this work, two types of simulations were considered: the first one assumes a concentrated flow of incoming particles (CF), and the second one considers the angular distribution of the sputtered Ti particles to approximate as closely as possible the conditions of magnetron sputtering (MS). At $\alpha \geq 35°$, the formation of separate high aspect ratio columns inclined in the direction of the incoming particle flow is observed for both types of particle flow. Column width, column slope, average layer density, and the compactness of TiN films exhibit an upward trend as the substrate temperature rises, primarily attributed to enhanced surface diffusion. In the case of CF, the column tilt angle β experiences a progressive increase from 3° to 60° as α increases. However, when considering the MS distribution, β stabilizes at approximately 35°. The connection between β and α, as well as their dependence on temperature, underwent thorough discussion and comparison with experimental findings.

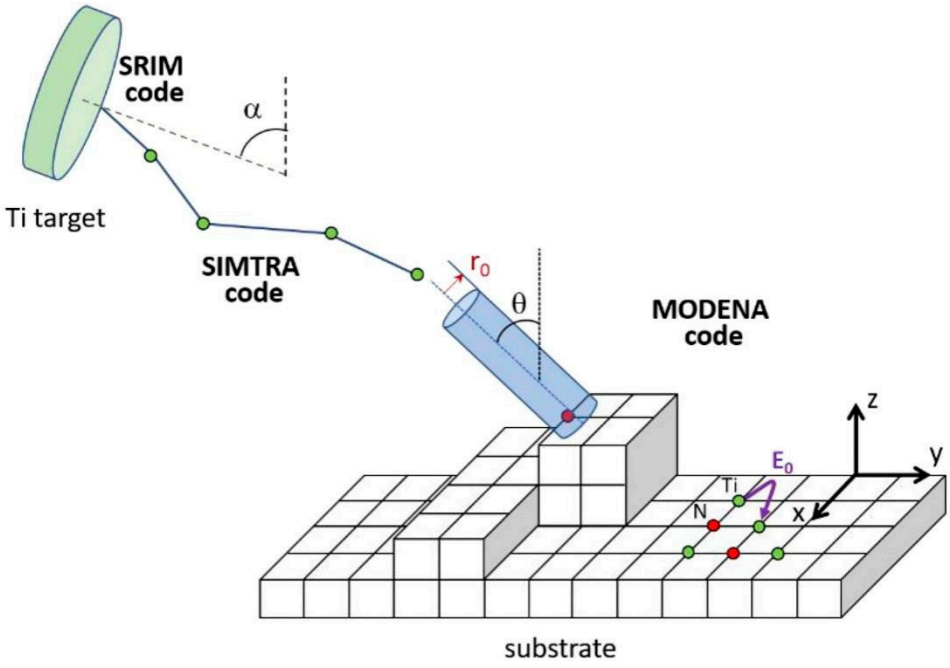

Figure 6. Schematic representation of the 3D model used for computer simulation of the growth morphology of the tilt at a certain angle TiN film by the KMC method [50].

A KMC simulation of the ALD process using $TiCl_4$ and NH_3 precursors was given in [51]. Key reactions relevant to the ALD process, such as precursor adsorption/desorption, formation of surface Cl atoms, and evolution of free HCl and Cl_2 molecules, were deduced based on a lattice model. Reaction energies were calculated based on DFT considering the local environment, while activation barriers are linearly fitted to sample cases from different reaction families. The growth rate and number of Cl residues agree with the experiment, indicating that the model represents the key chemical reactions well. A detailed growth mechanism was demonstrated and the critical role of surface Cl atoms, which dissociate from $TiCl_4$ in the ALD process through the formation of HCl gas, was highlighted.

2.2. Molecular Dynamics Simulation

2.2.1. VN, TiN

Researchers are highly intrigued by transition metal nitrides like vanadium nitride (VN), titanium nitride (TiN), and niobium nitride (NbN) due to their extraordinary physical

and mechanical characteristics. These properties encompass exceptional wear resistance, superhardness, and thermal stability. These remarkable traits are typically achieved through the alternating nanolayers of different nitrides, making them a subject of significant interest [52]. For example, in work [53], hardness higher than 50 GPa was obtained for the TiN/VN structure. In [52], a modified method of "embedded" atom was used to describe V–V, N–N, and V–N interactions, as well as the Lennard-Jones potential for C–N and C–V pairs was utilized. Based on these potentials, MD simulation of the "VN thin film (001)—columnar diamond indenter" system was carried out and the evolution of the structure during indentation was investigated with centrosymmetry parameters and atomic configurations of VN film sections. The slipping in VN films during indentation occurred along the {110} 110 direction at the initial stage. As the indentation depth increased, some of the slips also occurred in the {111} 110 and {100} 011 directions. The model was extended in [54,55]. The formation of deformation twins, the initial plastic deformation, and the mechanisms of the formation of dislocation loops during nanoindentation were studied.

TiN_x compounds (where x can take values from 0.6 to 1.0) are not only one of the most widely used materials as hard coatings, but also serve as a model system for nitride compounds and alloys with the NaCl structure [56]. TiN is widely studied experimentally to identify patterns of formation of nuclei, their growth, and microstructure evolution [5,56,57].

One of the first research works studying the interatomic potentials in metal nitrides is [20], where the parameters for the Mie-Gruneisen, Morse, and Buckingham pair potentials were calculated, and their correspondence to the real properties of the mentioned compounds was analyzed. A pair potential for TiN developed based on the DFT was proposed in [58]. The potential was formulated as the summation of two components: a long-range component represented in Coulombic form, and a short-range component that encompassed the remaining energy contributions. It should be noted that pair-type potentials have serious limitations and are unable to realistically describe the basic set of physical and chemical properties, in particular to provide a reference structure.

In [59], the Tersoff many-body potential was already developed for calculating the adhesion energy of the metal/dielectric and metal/metal interface. In works [19,21], the modified method of "embedded" atom (2NN-MEAM) was adapted to the Ti-N pair. The potentials with the parameters calculated in these works showed good agreement with the experimental data, although they showed certain deviations in the cohesion energies and atomic structure.

Further development of the 2NN-MEAM potential for the Ti-N system, where it was combined with the ZBL potential for a realistic description of short-range repulsive interatomic interactions during the atomic deposition process, was carried out in the work [60] (Figure 7). The influence of the substrate temperature (300–700 K) and the energy of depositing atoms (2–10 eV) on the concentration of defects in the film and its stoichiometry was investigated. At the same time, only 550 ps of system evolution were simulated, which is not enough to detect all effects at a realistic flux density.

A large-scale classical MD simulation of TiN/TiN(001) epitaxy at 1200 K was carried out [56] under the conditions of incident flux ratios N:Ti = 1, 2, and 4 to study the stoichiometry, island size distribution, island boundary orientations, and formation vacancies in the early stages of film growth. The films were generally not sufficiently stoichiometric at low N:Ti ratios, with surfaces that contain 111-oriented sites with a high content of Ti atoms. Multilayer growth prevails, and mainly 100-oriented epitaxial islands were formed in this mode. As N:Ti increases, 110-oriented islands of N atoms at the edges become increasingly dominant. Deposition with the ratios N:Ti = 2 and 4 leads to films whose growth mode is closer to the ideal layer-by-layer case. The films were almost stoichiometric with an excess of N atoms, which are located on the boundaries of polar 110-oriented islands (see Figure 8).

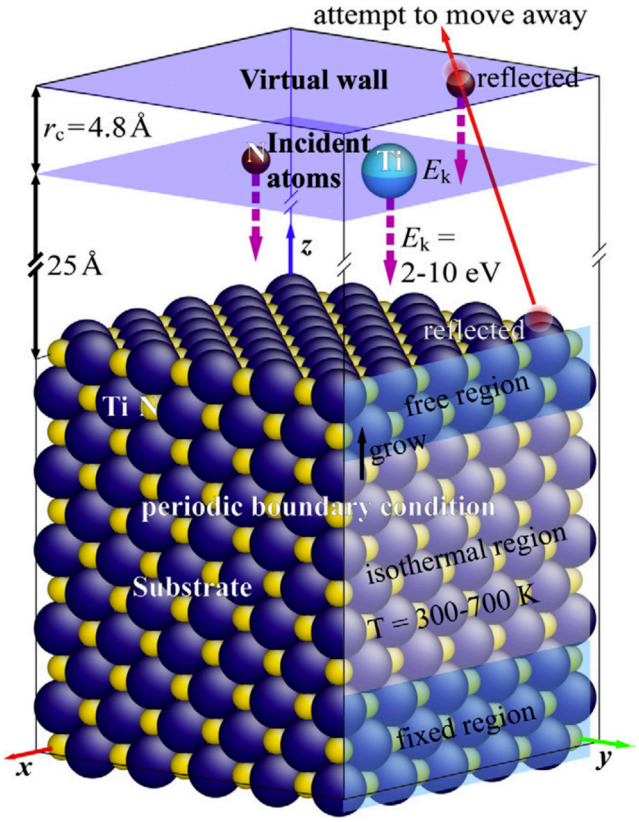

Figure 7. Scheme of the MD model of atomic deposition [60].

The study of film growth modes was also carried out in [61], where the influence of the energy of depositing atoms on the nature of film growth was shown. The results showed that low energies lead to the formation of "islands". At the same time, high-energy atoms form a layer-by-layer film. The boundary between the substrate and the film gives rise to an attractive force due to the lattice mismatch between the well-ordered substrate and the initial formation of "islands" in the coating. The tensile force experienced by surface atoms in the film is generated by internally structured atoms.

The deposition of a Ti–TiN multilayer coating on an FeCrNi substrate was simulated in [62]. Two-layer (TI–TiN) and four-layer (Ti–TiN–Ti–TiN) coatings were studied. Also, stresses and cohesion energies were calculated.

2.2.2. TaN

In works [63–65], the Morse pair potential was used. The parameters for the interaction between Ta and N atoms were calculated using the Lorentz–Berthelot mixing rules.

2.2.3. ZrN

The application of ZnN and MoN coatings is also promising as well as other nitride coatings, because they demonstrate high hardness, corrosion resistance, etc. Multilayer structures such as TiN/ZrN [66] and TiN/MoN [67] are particularly interesting. In [66], an ab initio MD approach was used to model the evolution of a multilayer structure of 6 layers of TiN (111) and 6 layers of ZrN (111), as well as a structure of 12 layers of ZrN (111). The findings reveal that the ideal tensile strength of the multilayer structure is lower when compared to the individual ideal tensile strengths of TiN and ZrN. This suggests that the formation of a multilayer heterostructure does not result in its strengthening in terms of chemical bonds. Drawing from both experimental and theoretical research, it can be inferred that the strength of TiN/ZrN nanolayer films improves due to the presence of TiN/ZrN interfaces that hinder the dislocation movement, along with a preference for (111) crystal orientation.

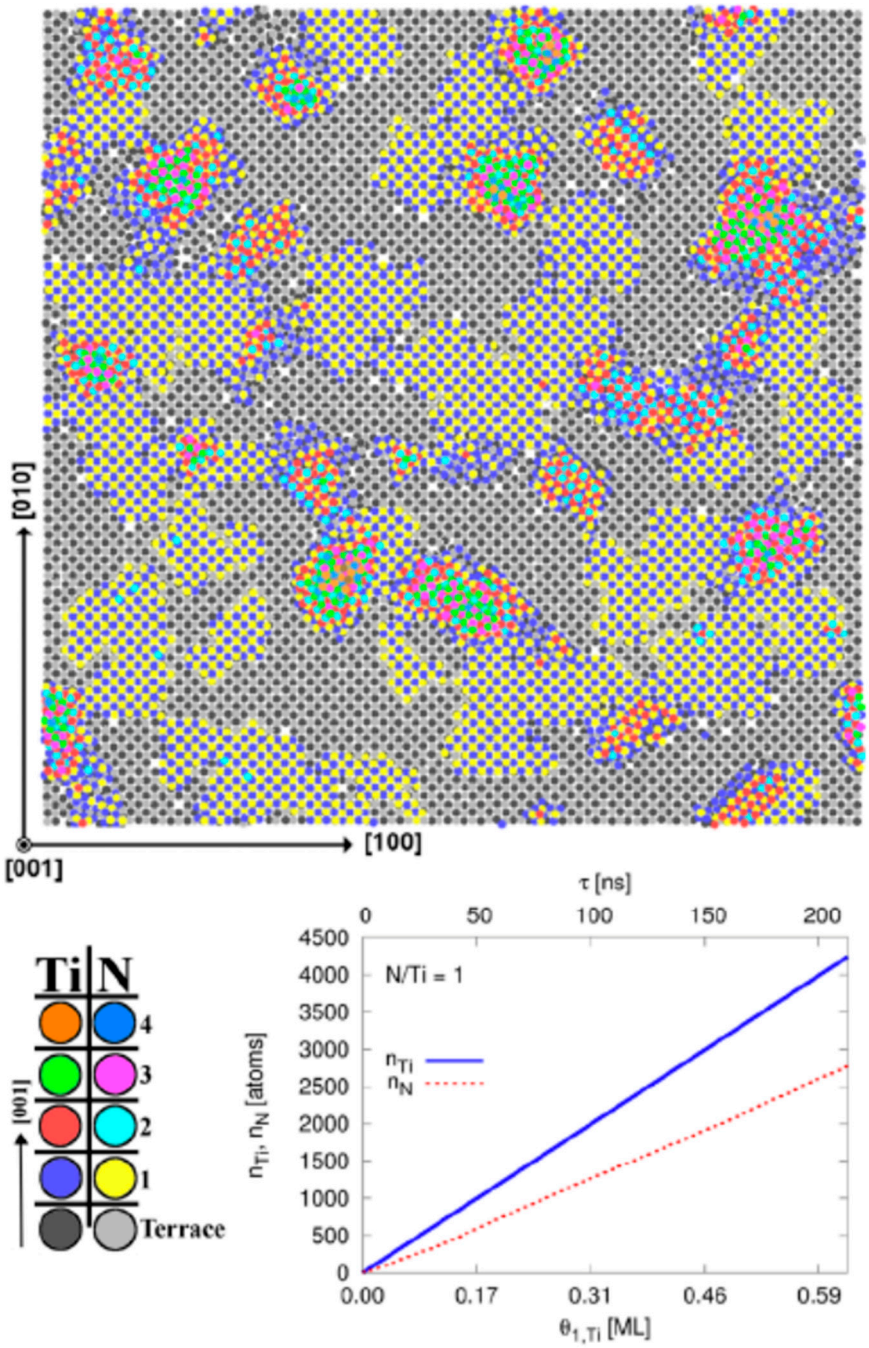

Figure 8. Location of all deposited atoms (top layers) along 001 during the growth of TiN/TiN(001) film at 1200 K after deposition of 4250 Ti atoms with N:Ti = 1 ratio [56].

2.2.4. FeN

Iron nitrides, in particular, Fe_4N, are widely used in high-density magnetic storage devices. This causes significant interest in studying their magnetic properties, which, in turn, depend on the phase [68]. Nitrides are nonmagnetic for cubic phases of the γ″-ZnS type, while the γ″-NaCl type is antiferromagnetic. Iron nitrides located within the iron-rich side of the phase diagram predominantly exhibit ferromagnetic properties. In [69], ab initio MD (VASP package) was used to simulate FeN films on a Cu (100) substrate. The process of nitride film formation begins with the interaction of nitrogen and iron atoms on the two upper layers. Then, a joint up and down movement of iron and nitrogen atoms over the substrate is performed until equilibrium is reached. At the same time, it was noted

that the simulation time was sufficient for complete relaxation of these processes. In terms of magnetic properties, the results show that the iron nitride thin films are ferromagnetic with a magnetic moment of 1.69 μB, 2.14 μB, and 2.21 μB for the first three layers. These magnetization trends during simulation correspond to the experimental results.

In [70], classical MD based on the MEAM potential was applied to study the evolution of γ″-Fe_4N and α″-$Fe_{16}N_2$. As a result of the simulation, realistic lattice templates for the corresponding phases were obtained, which will be useful for further studies of magnetic and other properties at the atomic-discrete approximation.

2.2.5. CrN

In [71], a computational model based on the MD method for simulation of the process of nanoindentation of solid materials using Morse pair potential was developed. This model was employed to replicate the mechanical characteristics of thin film systems that comprise Cr/CrN and $(Cr/CrN)_2$. The stiffness values were calculated using both the Oliver-Parr and Cheng correction techniques. The modulus of elasticity of the Cr/CrN and $(Cr/CrN)_2$ films was 217.86 GPa and 258.9 GPa, respectively. The influence of temperature on the systems was also studied. According to the results, stiffness decreases with the increasing temperature. It is related to instabilities in the crystal structure caused by changes in the positions of atoms due to the instantaneous kinetic energy of each particle which is of a thermal nature. Nevertheless, MD methods have a wider range of applications, namely, they can be used to study the mechanical properties of corresponding films.

In [72], CrN coatings, in particular oxidation processes, were investigated using DFT combined with AIMD in the CASTEP package. The surface energy, adsorption configuration, and electronic structure of molecules and oxygen atoms on the CrN (100) surface were studied using DFT calculations. AIMD calculations were used to study the evolution of the geometric configuration and electronic structure of the adsorption process and dissociation of the O_2 molecule at 1073 K.

2.2.6. Ternary Alloys

The TiAlN alloy appears to be a promising coating, which in addition to hardness also shows resistance to oxidation with an increase in Al concentration. In [73], ab initio MD simulation (VASP package) of TiAlN coating during interaction with O atoms at different temperatures and different Ti:Al ratios was carried out using the generalized gradient approximation (GGA) and the projector method with augmented plane wave (PAW). The elasticity of TiAlN was successfully modeled using special quasi-random structures (SQSs) [74] generated for NaCl-structured TiAlN solid solutions by the mcsqs program, which is a part of the ATAT package.

Quantum MD methods were used [75] to confirm the experimental results of magnetron sputtering of Nb-Si-N films. The ESPRESSO quantum code with periodic boundary conditions and the general gradient approximation (GGA) for exchange-correlation energy was used for quantum mechanical calculations. The interaction of electrons with ions was simulated by Vanderbilt pseudopotentials using ultra-soft modes [76]. The initial structure was optimized by simultaneous relaxation of the basis vectors and atomic positions within the cell using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. MD simulations provided an understanding of the structure that causes the increase in hardness values (~32 GPa) for Nb-Si-N coatings compared to NbN (~28 GPa).

3. Conclusions

Today, the main atomic-discrete approaches to modeling the thin film formation of metal compounds are Monte Carlo, molecular dynamics, as well as hybrid versions comprising different combinations of the above methods and elements of analytical descriptions. Molecular dynamics methods are more accurate, but the Monte Carlo method allows for simulations to be carried out over a longer time, which becomes critical given the typical times of the film deposition process. Therefore, the most promising option is the use of com-

bined methods and accelerated molecular dynamics. The accelerated dynamics methods allow for increasing the available simulation times by orders of magnitude in the case of an acceptable selection of model parameters for the systems with relatively "rare" thermally activated atomic relocation events. The implementation of the latter approach is considered by the authors as the near-term prospect of research on simulating the deposition of nitride coatings. The considered models can be used to model films of other metal compounds, in particular carbides and borides.

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