Molecular dynamics simulation of Ni thin films on Cu and Au under nanoindentation

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The deposition and indentation process in Ni/Au and Ni/Cu systems were studied. Growth of Ni films on Cu and Au substrate were modelled to obtain systems for indentation. These systems during deposition and indentation were evaluated by employing molecular dynamics simulation with potentials based on the embedded atom method theory. Additionally, two body Morse potentials was included to simulation of indentation process and a rigid spherical indenter with the diamond structure was used. Adaptive common neighbour analysis and centrosymmetry parameter were applied to the structural characterisation of deposited layers. During the deposition the stress gradually reaches a constant value and directly correlate with structural changes in the deposited layers. The Ni layer deposited on the Cu forms a BCC structure, but in the case of deposition on Au, a HCP structure intersected by the boundaries was formed. The increase of hardness in Ni deposited films is linked with the decreasing thickness of a thermal layer in the system. A correlation between structure and distribution of deformation in the Ni/Cu and Ni/Au systems were found. The plastic deformation in the Ni/Cu systems propagates uniformly from the centre of indentation, but for Ni/Au propagates along the grain boundaries, additionally.

1. Introduction

Thin films, material layers with thicknesses of a few nanometers, find several different technological applications including, for example, hard/tough wear-resistant protective coatings in industrial machining [1,2], photovoltaics [3,4], electronics [5,6], and energy storage [7,8]. For each application, the thin film mechanical properties need to be tailored to specific operative conditions, thus preserving tool or device performances and extending their lifetimes. The mechanical properties are, in turn, strongly affected by the coating or thin-film material thicknesses [9—11], thermal stability [12,13], roughness [14,15], structure defects [16], and texture [17]. For ceramic electrically conductive crystalline systems, for instance, the control of stoichiometry (e.g. lattice vacancies), is used to tune elasticity [18], hardness [19,20] and/or toughness [21] together with phase stability [22] as well as optical [23] and electrical/thermal transport [24,25] properties.

Nanotechnology leads to the development of devices whose structure and function are controlled at the atomic level. Therefore,

understanding the properties from the atomic point of view is important for the development of such systems [26,27]. Thin-layer systems are produced in Ultra High Vacuum (UHV) systems. Application of different methods and parameters of deposition leads to systems with different physical properties [28,29]. Also different techniques of modification allow to obtain layers that have different stresses [30]. Particularly, the change in internal layer stress leads to changes in the structure and mechanical properties of systems such as hardness and modulus of elasticity.

Nanoindentation has been a subject of intensive experimental and theoretical study [31—38]. Nanoindentation is a commonly used technique for probing mechanical properties, especially surfaces and thin films. From the shape of the force-distance curve information about the elastic modulus and hardness can be obtained [39].

Deformation mechanisms of nanocrystal materials have been investigated extensively using Molecular Dynamics (MD) simulation [34,36,37]. Given that first-principles *ab initio* molecular dynamics (AIMD) [40] is generally too computationally demanding for determining the evolution of large systems. MD simulations are typically based on efficient empirical-model interatomic potentials [41—44] fitted to *ab initio* or experimental results. Thus, their

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reliability is always subject to preliminary benchmarking. However, validated with respect to experiments or AIMD simulations for relatively small systems [45–47], classical MD simulations are an indispensable predictive computational tool which allows discovering novel reaction mechanism with corresponding rates at environmental conditions of interest [48–50], as well as to realistically simulate crystal synthesis or thin film growth [51,52]. In the work [34], the authors use MD simulation to perform nanoindentation on pure gold and on gold alloys with various crystal surfaces. The authors analyse the plots of hardness vs. force and show that the existing characteristic peaks correspond to defect nucleation in the structure. They found that yield strength for various crystallographic orientation calculated from the embedded atom method (EAM) potentials corresponds to the results obtained from experiments [35]. Study [36] presents the effect of temperature on the hardness of the Cu/Ni system. The authors investigated the influence of temperature on surface roughness and hardness of systems before and after annealing. They found that higher temperature eliminates defects in the structure of the systems and increases their hardness. However, in study [37], nanoindentation of the Al/Ni multilayer was studied. The authors investigated the influence of grain size, the grain morphology and the thickness of deposited layers on the elastic modulus and hardness. They found that in nanocrystalline Al/Ni multilayer hardness and elastic modulus decrease with refinement of grain size. In the Al/Ni system, hardness is more affected by the layer thickness than the grain size.

The aim of this work is to study correlation between structure and hardness in Ni/Au and Ni/Cu systems. The deposition process and the behaviour of these systems are evaluated by employing molecular dynamics simulation using potentials described by the embedded atom method and Morse potential. To simulate the indentation process we used a rigid spherical diamond indenter. To investigate the structure in Ni/Au and Ni/Cu systems, the adaptive common neighbour analysis (ACNA) method and the centrosymmetry parameter (CSP) were applied. The stress was determined by the Basinski, Duesberry, and Taylor (BDT) atomic stress definition.

2. Simulation method

Molecular dynamics simulation of deposition and the indentation models were applied and are presented in Fig. 1. Before the indentation process, the samples of Ni deposited on the Cu and Au substrate were prepared. For deposition, the initial systems are composed of an unmovable substrate and thermal layers of the same metal. These layers are assumed to be the (001) plane of FCC regular crystal with bulk crystal lattice constants equal to $a_{Au} = 4.08$ Å and $a_{Cu} = 3.62$ Å. In contrast to the substrate, the atoms in the thermal layers can change their position during simulation. Before the deposition process, the thermal layers were equilibrated at a desired temperature. The rectangular simulation box has the size 134.64 Å × 134.64 Å × 40.00 Å for the Au substrate and 130.32 Å × 130.32 Å × 40.00 Å for the Cu substrate along the x, y and z directions, respectively. In all simulation, the periodic boundary conditions were applied in x and y directions. The time step was $\Delta t = 0.005$ ps and the deposition rate V of atoms was equal to one deposited atom per two thousand simulation steps. The temperature during deposition was equal to 300 K, and the energy of deposition was always 1eV. The deposited atoms and the atoms in the thermal layer are under thermal control and the temperature during the simulation was kept fixed by periodical velocity rescaling every five timesteps. To prevent the atoms from leaving the simulation box in deposition, a reflecting wall was placed at its top. The deposition process was divided into two stages. At first, the particles were created at random (x, y) positions and initially oriented perpendicular to the bottom surface. Next, the system obtained was equilibrated by periodical velocity rescaling. The system thus prepared was subjected to the indentation process. Before indentation all systems were equilibrated by periodical velocity rescaling to 300 K, giving a system with roughness which did not affected on indentation results. The diamond indenter sphere is treated as being rigid and is placed at 5 Å above the top surface. The force acting on an individual particle of an indenter is calculated by summing the force contribution of the surrounding atoms. The hardness was obtained from relation:

$$H = \frac{F_{ind}}{\pi(2Rd - d^2)} \tag{1}$$

where F_{ind} is average force acting on an indenter, R is the radius of the intender and d is indentation depth. Indentation tests were performed with the spherical indenter of 24 Å in diameter at a constant indenting speed of 50 m/s. The maximum depth was set to 12 Å.

In our simulation the interactions between metal atoms were described by EAM potential [53]. In the EAM, the total energy E can be expressed as:

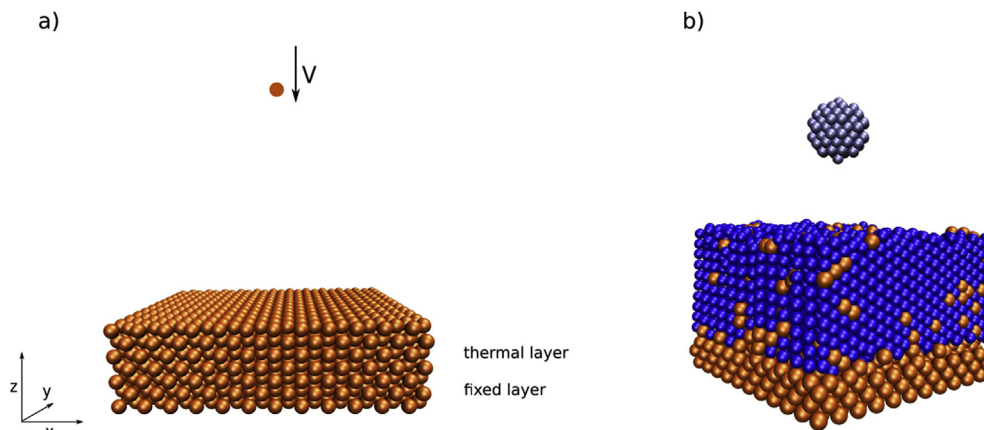$$E = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i,j(i \neq j)} \phi_{ij}(r_{ij}), \rho_i = \sum_j f(r_{ij}) \tag{2}$$

a)

b)

Fig. 1. The simulation model for (a) deposition process and (b) indentation process.