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**TiN film growth on misoriented TiN grains with simultaneous low-energy bombardment: restructuring leading to epitaxy**

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**Abstract**

We perform large-scale molecular dynamics simulations of TiN deposition at 1200 K on TiN substrates consisting of under-stoichiometric ( $N/Ti = 0.86$ ) misoriented grains. The energy of incoming Ti atoms is 2 eV and that of incoming N atoms is 10 eV. The simulations show that misoriented grains are reoriented during the early stages of growth, after which the film grows 001 epitaxially and is nearly stoichiometric. The grain reorientation coincides with an increase in film N/Ti ratio. As the grains reorient, additional nitrogen can no longer be accommodated, and the film composition becomes stoichiometric as the overlayer grows epitaxially.

## 1. Introduction

Transition-metal (TM) nitride [1–3] thin films are employed in a wide variety of applications due to their unique combination of properties including high hardness, [1,4–6] scratch and abrasion resistance, [7] low coefficient of friction, [8] high-temperature oxidation resistance, [9–11] metallic-to-semiconducting electrical conductivity, [12–15] optical absorption which is tunable across the visible spectrum, [16,17] biocompatibility, [18] and superconductivity. [12,19,20]  $\text{TiN}_x$ , with a single-phase field ranging from  $x = 0.6$  to  $1.0$ , [21] was one of the first hard-coating materials and today serves as a model system for investigating NaCl-structure TM nitride compounds and alloys. Consequently, TiN has been extensively studied experimentally in order to probe nucleation and island formation, [22,23] growth kinetics, [24–27] and microstructure and texture evolution. [28–40]

Fundamental understanding of the processes governing nanostructural and surface morphological evolution during thin-film growth requires detailed information regarding the dynamics of mass transport on surfaces, nucleation, and the early stages of growth. Since surface processes occurring on the picosecond time scale cannot be resolved with state-of-the-art atomic-scale experimental techniques, such as scanning tunneling microscopy [24,25,41] and low-energy electron microscopy, [42] the use of complementary computational investigations is essential. Conversely, while *ab-initio* computational methods such as density functional theory (DFT) have been successfully applied in studies of materials properties [43,44] and fundamental surface interactions, [45] the system sizes and time scales required for film-growth studies are prohibitively large for these methods. This renders methods such as Kinetic Monte Carlo (KMC) [46] and Classical Molecular Dynamics (CMD) [47,48] as the primary computational tool for large-scale studies of film growth dynamics.

We have previously applied CMD to investigate both intralayer and interlayer mass transport of Ti and N adatoms, and  $\text{TiN}_x$  ad molecules, on  $\text{TiN}(001)$  [49] and  $\text{TiN}(111)$  terraces

[50] as well as on TiN/TiN(001) islands. [51,52] Ti adatom migration velocities on infinite terraces at 1000 K are nearly three times that of N adatoms [49]. On TiN/TiN(001) islands, Ti adatoms rapidly reach island step edges and descend exclusively via push-out/exchange processes, whereas N adatoms have lower mobilities and descend by both hopping over step-edges and push-out/exchange with N edge atoms. [51] Admolecule surface mobilities depend strongly on the N-content of the molecule. While TiN<sub>2</sub> admolecules display remarkably high mobilities on both flat TiN(001) terraces and TiN/TiN(001) islands, TiN<sub>3</sub> admolecules remain essentially stationary. Motivated by these results, we performed a large-scale MD study of TiN/TiN(001) film growth using incident N/Ti ratios of  $N/Ti = 1, 2$ , and 4 to investigate the effect of the N/Ti ratio on film growth modes at 1200 K [53], a typical TiN/TiN(001) epitaxial growth temperature. [14,54] The results demonstrated that at low N/Ti flux ratios, both 100- and 110-bounded epitaxial islands are formed, and surface roughening occurs through nucleation of 111 islands in areas of local N deficiency via growth of 110-oriented in-plane ladder-like structures. At higher N/Ti ratios, islands with N-terminated 110 edges become dominant and surface roughening occurs due to enhanced upper-layer nucleation. Films grown with  $N/Ti = 2$  display the smoothest surfaces.

The reaction paths of incident N and Ti atoms on TiN(001) surfaces have been theoretically and experimentally shown to depend strongly on the incident kinetic energy [47,54]. The effect of the choice of incident energy was probed in a separate CMD study [55] in which TiN/TiN(001) films were grown at 1200 K using incident N energies  $E_N$  of 2 and 10 eV at a flux ratio of  $N/Ti = 4$ . The results showed that growth with  $E_N = 2$  eV results in globally overstoichiometric films with islands primarily bounded by N-terminated 110 edges; rapid upper-layer nucleation led to surface roughening. With  $E_N = 10$  eV, small islands were continuously dissociated into smaller clusters and adatoms leading to higher upper-layer

supersaturation, resulting in smoother films with compositions close to stoichiometric. Incident energetic N atoms also give rise to increased nitrogen desorption and reflection.

The large-scale CMD studies described above were designed to investigate the initial stages of growth, up to coverages of 0.85 and 1.5 monolayers, respectively. In both cases, the films were grown on perfectly smooth stoichiometric TiN(001) substrates. In this study, we investigate mechanisms by which low-energy ion irradiation affects TiN growth on a non-flat TiN substrate with misoriented grains. Using incident energies  $E_N = 10$  eV and  $E_{Ti} = 2$  eV, we simulate the growth of several monolayers of TiN. The results show that the initially misoriented grains are quickly restructured as energetic nitrogen is deposited; the resulting film is epitaxial.

## 2. Methodology

We perform large-scale CMD simulations of TiN/TiN(001) film growth at 1200 K, a temperature within the optimal range for TiN(001) epitaxial growth [14,54] with a N/Ti flux ratio of six and incident Ti and N energies of 2 and 10 eV, respectively. An energy of 2 eV corresponds approximately to thermal atoms accelerated by the surface potential of the substrate. [56] During dc magnetron sputter deposition of TiN in pure N<sub>2</sub>, ~96% of all incident ions are N<sub>2</sub><sup>+</sup> ions. With a typical floating potential of -20 V, the energy per atom upon dissociative impact will be 10 eV. [56] In previous MD studies, the use of N atoms incident at 10 eV energies resulted in smoother films, compared to 2 eV N, and compositions near stoichiometric. [55]

The simulations are carried out using the modified embedded-atom method (MEAM) [57] interatomic potential as implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [58] with the TiN parameterization employed in references [49,51,52,59,60]. The parameterization has been validated using DFT-based *ab-initio*

molecular dynamics to determine Ti [59] and N [60] diffusion kinetics on, as well as N<sub>2</sub> desorption from, [60] TiN(001) surfaces.

We use the film grown on an ideal NaCl-structure TiN(001) substrate consisting of 100 x 100 x 6 atoms with a nearest-neighbor interatomic stance of 2.121 Å, corresponding to a lattice constant of 4.242 Å, with  $E_{\text{Ti}} = E_{\text{N}} = 2$  eV and  $N/\text{Ti} = 1$  at 1200 K in the study detailed in our previous work [53] as the starting surface. The present substrate contains 67,018 atoms with an average grain size of 580 Å<sup>2</sup>. The N/Ti ratio at the substrate surface is 0.86, in which an atom is considered part of the surface if its z-coordinate is greater or equal to that of the top surface layer. An atomic-scale plan-view of the present substrate is shown in Figure 1. The misoriented grains (primarily 111), with a coverage of 0.18 ML are smaller than the 100-oriented grains, with an average grain size of 430 Å<sup>2</sup> compared to 760 Å<sup>2</sup> for 100-oriented grains.

The total simulation cell size is 212.1x212.1x65.6 Å, periodic boundary conditions are applied in the in-plane directions, and the simulation timesteps are 1 fs. Atoms in the bottom substrate layer are stationary, while atoms in the second, third, and fourth lowest layers are subject to velocity rescaling at each time-step and thus act as a heat sink to maintain the temperature constant at 1200 K. Atoms in the third layer and above, are free of any constraints. Every 100 timesteps, or 0.1 ps, we add a Ti atom and 6 N atoms, starting at random positions within 2 Å from the top of the simulation box, which corresponds to approximately 43 Å above the topmost substrate atom at the start of the simulation. The incident atoms are assigned a random velocity within a 30° angle from normal incidence corresponding to an average energy of 2 eV for Ti and 10 eV for N atoms. The range of incidence angles is used to approximate TiN deposition by magnetron sputtering, for which atoms are sputtered with a cosine distribution followed by ballistic transport through the gas phase. [61]

The coordinates of atoms belonging to the sixth layer and above are stored every 1,000 timesteps (1 ps) in MD videos which are visualized using Visual Molecular Dynamics. [62] In addition, the coordinates of *all* atoms in the simulation are stored every 150,000 timesteps (150 ps). We simulate  $\tau = 5.25$  ns of deposition time in which 52,500 Ti atoms are incident at the substrate and growing film. This corresponds, for unity Ti incorporation probability, to a nominal Ti sublattice coverage of 10.5 ML. Due to losses associated with incident-atom reflection and desorption, the actual final sublattice coverage is 9.81 ML, which corresponds to a growth rate of 1.87 ML/ns. During the initial 0.6 ns deposition time, we store the coordinates of all atoms every 25 fs in order to obtain a more detailed view of the initial growth stages. Atoms are free to leave the simulation box via direct reflection or through N<sub>2</sub> desorption as N adatoms bond with, and remove, N surface atoms. [47,60]

### 3. Results and Discussion

Figure 2 is a plot of the number of Ti and N atoms accommodated in the growing film (sixth layer and above), as a function of film coverage. Atoms in the fifth layer and below are considered part of the substrate. The corresponding film stoichiometry (N/Ti ratio) is also plotted on the right vertical axis. At the onset of deposition, the growing film is understoichiometric ( $N/Ti \approx 0.84$ ) due to the low N/Ti ratio in the substrate [53], TiN<sub>0.84</sub>. During film growth with  $N/Ti = 6$ , the film quickly becomes overstoichiometric, due to adsorption of N adatoms and formation of N-rich admolecules on the film surface, with a maximum  $N/Ti = 1.12$  after deposition of 1.4 ML. As deposition continues, the film stoichiometry stabilizes at TiN<sub>1.05</sub>.

Film growth on misoriented grains present in the initial substrate leads to mound formation, in contrast to the flat epitaxial islands which form on 100-oriented grains. However, the misoriented grains are eliminated during the early stages of deposition. Figure 3 shows the

evolution, in both plan view and cross-section, of the typical misoriented grain highlighted in Figure 1 during the initial 0.6 ns of deposition. The outline of the original misoriented grain is highlighted in white for each cross-section. In cross-sections (a)-(c), the grain boundary is highlighted in cyan. After reaching a coverage  $\theta$  of 0.61 ML, the misoriented grain is still present, but noticeably smaller. At  $\theta = 0.81$  ML, the grain size is significantly reduced. Interestingly, the reorientation does not appear to proceed from the top of the grain and into the film, but instead proceeds from within the grain toward the surface. The grain is completely reoriented to 001 at  $\theta = 1.13$  ML. Following deposition of 1.43 ML, the grain was allowed to relax for 0.15 ns without further deposition and it was found to remain stable in the 001 configuration. For completeness, we also show three snapshots of the film in the later stages of deposition. Figures 3(h)-(i), corresponding to  $\theta = 3.04$ , 5.74, and 9.81 ML, are cross-sections of the 001 layers grown on the initially misoriented 111 grain. Note the apparent formation of a pore in Fig. 3(i). Such pores are formed during film growth when two separate growing layers converge, giving the impression of a pore, which is filled as mobile Ti adatoms descend from upper layers.

To quantify the grain reorientation, we count the number of Ti film atoms in epitaxial positions according to the following method. We define a grid of ideal epitaxial positions with an inter-site distance  $d_{NN} = 2.121$  Å along in-plane directions. For each as-deposited Ti atom, we identify the closest ideal epitaxial site and calculate the distance. If the square of the distance exceeds  $0.06d_{NN}^2$ , the atom is considered in a non-epitaxial site; otherwise it is epitaxial.

The overall results of this analysis are plotted in Fig. 4 as the fraction of non-epitaxial film atoms vs total film coverage  $\theta$ . Initially, there is a slight increase in the fraction of non-epitaxial atoms, as recently-deposited Ti atoms have yet to reach stable positions. In addition, isolated Ti adatoms on TiN(001) are known to favor fourfold-hollow sites over epitaxial sites. [49,59] The non-epitaxial fraction reaches a maximum at  $\theta \approx 0.10$  ML, after which it decreases



throughout the remainder of film deposition and saturates at  $\theta \simeq 0.01$ . The non-epitaxial fraction does not reach zero since atoms are being deposited continuously. This demonstrates quantitatively that the misoriented grains present in the initial substrate, which formed during growth with thermal species, are reoriented, leading to epitaxial TiN overgrowth, during energetic deposition.

The mechanism of the grain reorientation is similar to that of grain growth driven by total grain-boundary minimization. The lower-surface-energy [63] 001-oriented grain consumes the misoriented grain, thus eliminating the boundary and decreasing the total surface energy. The probability of atoms crossing the grain-boundary is facilitated by increased lattice vibrations due to energetic N impact.

We note that the deposited coverage required for grain reorientation, 1.43 ML, matches that of the initial increase in film N/Ti ratio to the maximum value (Fig. 2). The misoriented grains, which are understoichiometric, consume the excess nitrogen. When the grains are completely reoriented, the film can no longer accommodate excess nitrogen and the N/Ti ratio stabilizes at a value which is essentially stoichiometric.

## **Conclusions**

We have performed large-scale molecular dynamics simulations of TiN thin film deposition at 1200 K on TiN substrates consisting of under-stoichiometric misoriented (primarily 111) grains. The N/Ti growth flux ratio is six with incident Ti and N energies of 2 and 10 eV, respectively. The results show that the substrates grains are quickly reoriented to 001 during the very early stages of deposition and the film proceeds to grow with an (001)/[100] epitaxial relationship to the substrate. The reorientation coincides with an increase in the film N/Ti ratio. When the film/substrate system is fully reoriented, the film can no longer

accommodate additional nitrogen and the film N/Ti ratio stabilizes at a value close to stoichiometry,  $\text{TiN}_{1.05}$ , as the film continues to grow epitaxially.

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## Figure Captions

Figure 1: Initial substrate, consisting of misoriented TiN grains, grown on TiN(001). Ti atoms are blue while N atoms are yellow. The dashed square in the upper right of the image shows a typical misoriented 111 grain. The dashed line within the square shows the cut along which the cross-sectional views are obtained.

Figure 2: Number of Ti and N atoms (left) in the growing TiN film plotted vs film coverage  $\theta$ . The right vertical axis shows the corresponding N/Ti ratio.

Figure 3: (a) – (g) Evolution of the misoriented 111 TiN grain highlighted in Figure 1 during the initial deposition. Ti atoms are blue while N atoms are yellow. Each panel shows both a plan view and a cross-sectional view of the grain along the cut defined in Figure 1. The original misoriented grain is outlined in white in each cross-section. The boundary between 001 and 111 orientations is highlighted with a cyan line in images (a)-(c). (a) Prior to deposition, (b)  $\theta = 0.61$  ML, (c)  $\theta = 0.82$  ML, (d)  $\theta = 1.13$  ML, (e)  $\theta = 1.43$  ML, (f)  $\theta = 1.43$  ML followed by 0.15 ns of relaxation, (g)  $\theta = 3.04$  ML, (h)  $\theta = 5.74$  ML, and (i)  $\theta = 9.81$  ML.

Figure 4: Fraction of non-epitaxial Ti atoms versus TiN film coverage  $\theta$ .













