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Electronic Supplementary Information

Thermodynamic insights from interfacial interactions in TiN/amorphous Al_2O_3 heterostructures: Ab initio molecular dynamics and first principles investigation

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This supporting information explains the detailed methodology used to compute the elastic constants of amorphous films.

1. Preparation of the am-Al_2O_3 Substrate.

To properly accommodate an anisotropic cubic and isotropic amorphous TiN films on am-Al_2O_3 substrate, we constructed am-Al_2O_3 structures that are su□ciently large and similar in magnitude. The a and b directions are required to be long enough because there should exist enough space above the substrate for a representative film to be inserted. As artificial correlations over the periodic boundaries vanish within approximately 8.5 to 12 Å for all interfaces, we found that am-Al_2O_3 slab configurations with a = 11.793 Å for am-TiN (80-atoms), a = 8.518 Å for cubic-TiN(001) (46-atoms), a = 12.046 Å, b = 12.777 Å for cubic-TiN(011) (144-atoms), and a = 12.046 Å, b = 10.432 Å for cubic-TiN(111) (69-atoms), respectively, are sufficiently large to accommodate a representative TiN films above. In the z direction, the substrate is composed of a thickness of 11.793 Å. The height of the simulation cell in the z direction is fixed at 35 Å, providing a large vacuum of at least 18 Å when amorphous or crystalline films are inserted above the am-Al_2O_3 substrate.

AIMD simulations are carried out to obtain the am-Al_2O_3 structures. The cubic supercell with the density of 3.4 g/cm^3 was used, which is well matched to the value of the density (3.05 ~ 3.4 g/cm^3) for the amorphous Al_2O_3 in experiments.[1,2] As the a and b dimensions match the subsequent TiN films, this process ensures that any subsequent TiN film derived from the liquid does not develop artificial strains when transferring all TiN films onto the substrate. MD simulation was performed in the NVT ensemble for the liquid corresponding to the amorphous film considered (80 atoms) at 4000 K for 5000 MD steps, with a 1 fs time step. In the second (production) stage, the liquid is simulated for an additional 5000 MD steps.

2. Preparation of Amorphous TiN Film/am-Al_2O_3 Substrate Configurations.

For the amorphous TiN films, we start by creating a TiN liquid using AIMD in a cubic box. MD simulation is run in the NVT ensemble for the liquid amorphous film considered (96 atoms) at 4000 K for 5000 MD steps, with 1 fs time step. In the second (production) stage, the surface structure is simulated for an additional 5000 MD steps. These selected configurations are then transferred on to the am-Al_2O_3 slab, utilizing their existing atomic arrangements near the boundaries of their initial simulation box as the new film/substrate system. This procedure is equivalent to cleaving the configurations of bulk amorphous structure at a random position to create an interface with TiN surface and am-Al_2O_3 surface. At the end of this MD optimization, structural optimization using higher precision DFT-based conjugate-gradient is carried out to acquire the final energies of the supercells. Thinner films are created by removing stoichiometric portions of TiN from the top of the films and repeating the AIMD + DFT optimization routine as described above. For each film thickness, the configuration yielding the lowest energy is selected for further comparisons of stability.

3. Preparation of Cubic TiN Film/ am-Al_2O_3 Substrate Configurations.

TiN(001), TiN(011) and TiN(111) surfaces with B1-NaCl structure are used as the subsequent surfaces. The optimized lattice parameter of TiN is a_0 = 4.21 Å, which is in good agreement with the experimental value (a_0 = 4.24 Å).[3] For the TiN(001) surface, a slab of (2 x 2) supercell was considered. For comparison, the TiN(011) and TiN(111) surfaces were considered with a slab of (2 x 2) and (2 x 3) supercells, respectively.

4. Calculation of stability of each hetero-structure model.

For investigating the stability of each hetero-structure model, the interface formation energy was computed by the following formula:

$$E_{int} = -\left(E(TiN) + E(Al_2O_3) - E(TiN/Al_2O_3)\right)/S$$

E(TiN), E(Al_2O_3), and E(TiN/Al_2O_3) represent the total energies of the unrelaxed TiN slab, Al_2O_3 slab, and TiN/Al_2O_3 hetero-structure, respectively; and S is the area of the interface.

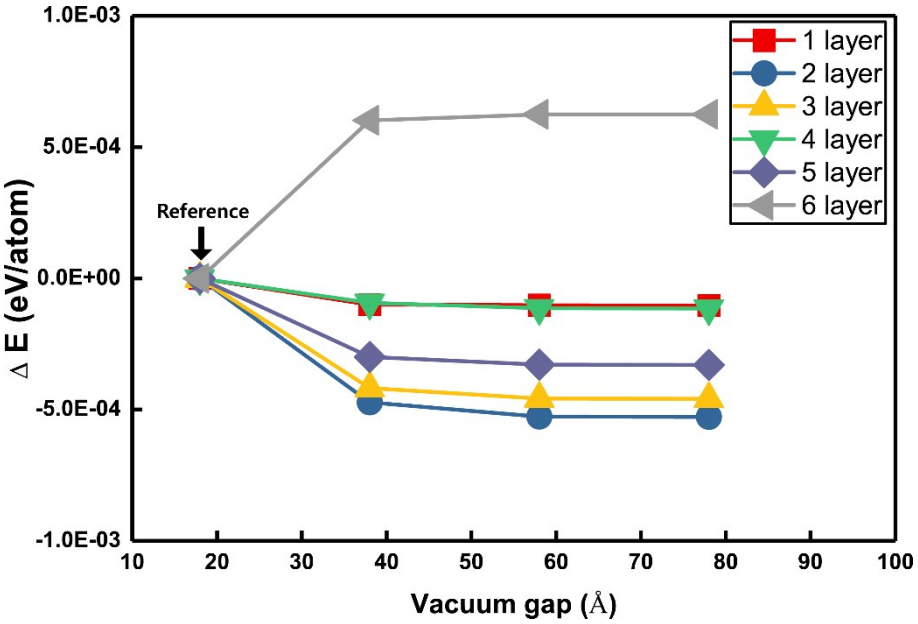

Figure S1. The energy difference between changed energy value (78 Å vacuum gap) and reference value (18 Å vacuum gap) for all TiN(111) layers on am-Al_2O_3 (OH-terminated).

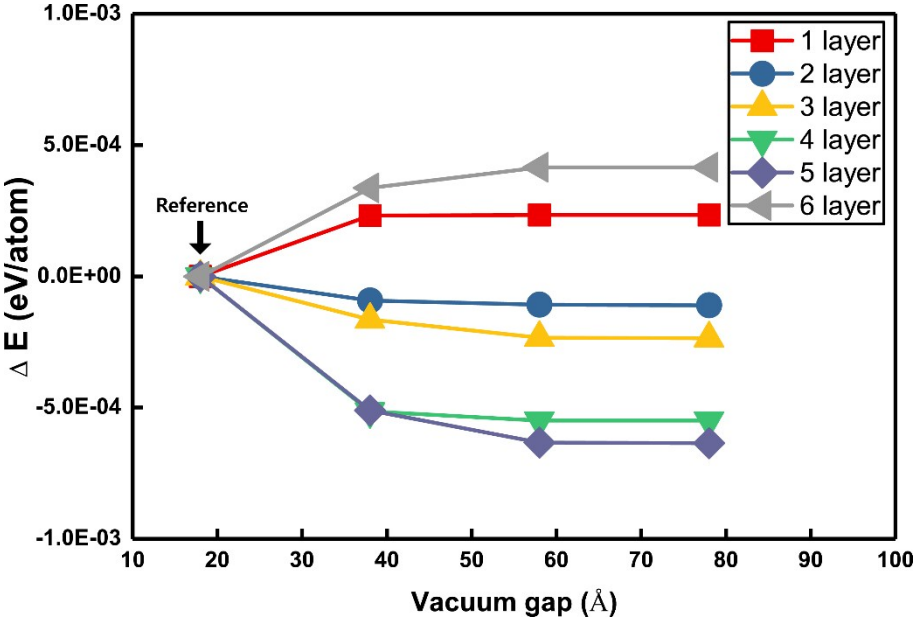

Figure S2. The energy difference between changed energy value (78 Å vacuum gap) and reference value (18 Å vacuum gap) for all TiN(111) layers on am-Al_2O_3 (O-terminated).

References

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