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Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Davide Sangiovanni, Björn Alling, Peter Steneteg, Lars Hultman and Igor Abrikosov, Nitrogen vacancy, self-interstitial diffusion, and Frenkel-pair formation/dissociation in B1 TiN studied by ab initio and classical molecular dynamics with optimized potentials, 2015, Physical Review B. Condensed Matter and Materials Physics, (91), 5, 054301.

<http://dx.doi.org/10.1103/PhysRevB.91.054301>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-114567>

Nitrogen vacancy, self-interstitial diffusion, and Frenkel-pair formation/dissociation in *B1* TiN studied by *ab initio* and classical molecular dynamics with optimized potentials

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(Received 25 August 2014; revised manuscript received 7 January 2015; published 2 February 2015)

We use *ab initio* and classical molecular dynamics (AIMD and CMD) based on the modified embedded-atom method (MEAM) potential to simulate diffusion of N vacancy and N self-interstitial point defects in *B1* TiN. TiN MEAM parameters are optimized to obtain CMD nitrogen point-defect jump rates in agreement with AIMD predictions, as well as an excellent description of TiN_x ($\sim 0.7 < x \leq 1$) elastic, thermal, and structural properties. We determine N dilute-point-defect diffusion pathways, activation energies, attempt frequencies, and diffusion coefficients as a function of temperature. In addition, the MD simulations presented in this paper reveal an unanticipated atomistic process, which controls the spontaneous formation of N self-interstitial/N vacancy ($\text{N}^{\text{I}}/\text{N}^{\text{V}}$) pairs (Frenkel pairs), in defect-free TiN. This entails that the N lattice atom leaves its bulk position and bonds to a neighboring N lattice atom. In most cases, Frenkel-pair N^{I} and N^{V} recombine within a fraction of ns; $\sim 50\%$ of these processes result in the exchange of two nitrogen lattice atoms ($\text{N}-\text{N}^{\text{Exc}}$). Occasionally, however, Frenkel-pair N-interstitial atoms permanently escape from the anion vacancy site, thus producing unpaired N^{I} and N^{V} point defects.

DOI: [10.1103/PhysRevB.91.054301](https://doi.org/10.1103/PhysRevB.91.054301)

PACS number(s): 81.05.Je, 66.30.Lw, 83.10.Rs, 71.15.Mb

I. INTRODUCTION

Due to excellent physical and mechanical properties, including high hardness [1–3] and toughness [4,5], chemical inertness [6], thermal stability [7], and good electrical conductivity [3], transition metal (TM) nitrides are widely applied as wear-resistant protective coatings for cutting tools [8] and engine components [9] and as diffusion barriers in electronic devices [10,11]. The properties and performances of TM nitride thin films depend on their micro- and nanostructure. The microstructural evolution occurring during synthesis and use, such as texture formation and phase separation upon alloying, is closely connected to the concentration and mobility of lattice defects.

To date, very little is known about the mass transport properties of TM nitride systems [12–14]. Even for TiN, the most well-characterized and widely applied TM nitride material [15], diffusion coefficients measured for bulk range over three to four orders of magnitude [14,16–18], because many physical parameters, including the relative concentration and spatial distribution of point defects, chemical composition, microstructure, residual stress, and presence of impurities, affect the experimental results. Theoretical methods can be used to interpret and guide experiments by separately probing the influence that each of the parameters mentioned above has on atomic diffusion.

Ab initio calculations focusing on atomic diffusion in bulk TiN [19] and on TiN [20,21] and TiAlN [22,23] surfaces have been used to estimate minimum energy paths and corresponding diffusion barriers at 0 K. Generally, this is accomplished by using algorithms, such as the nudged elastic band (NEB) method [24,25]. However, diffusion activation energies and related pathways are affected by lattice vibrations

at finite temperatures [26,27]. Moreover, the rate of thermally-activated migration events, which determines the value of diffusion coefficients, depends not only on diffusion energy barriers but also on jump attempt frequencies [28]. Vineyard showed that the latter can be estimated within the harmonic approximation at 0 K from the ratio of the product of the n phonon frequencies at the starting point of the transition to the $n - 1$ normal modes of the system constrained in the transition-state saddle-point configuration [29]. Such an approach, however, is not sufficiently accurate to describe materials characterized by largely anharmonic interactions [30]. Molecular dynamics (MD), which inherently resolves the problems mentioned above, is the most reliable method available to determine diffusion jump rates and migration pathways, and even discover nonintuitive diffusion mechanisms at finite temperatures, given that the computational challenges of long time scales can be resolved.

In MD simulations, the atomic interactions are described either from first-principle or by empirical mathematical functions. Both methods have their advantages and disadvantages. Density functional theory (DFT) is the most accurate methodology available to evaluate interatomic forces during first principles or *ab initio* MD (AIMD) runs at a reasonable computational cost [31]. However, the common approximations used in DFT for the estimation of the electron exchange and correlation energies, benchmarked primarily for defect-free crystalline solid systems [32], may yield less accurate interatomic forces between point-defect/host-lattice-atoms due to, e.g., more abrupt electron-density variations in the vicinity of vacancy sites [33]. In addition, highly computationally demanding AIMD based on DFT is confined to the simulation of small systems (a few hundred atoms) for short time intervals (a few nanoseconds). Thus, it is practically unfeasible to use this technique to observe diffusion processes at low temperatures, probe the effect of phonon wavelength degrees of freedom (varying supercell sizes) on

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atomic mobility, and estimate the effect of correlated jumps on diffusion coefficients. These limitations are overcome by using classical MD (CMD), as this requires considerably less computational resources than AIMD. However, the reliability of CMD predictions strongly depends on the applicability of the model potential to the material system of interest [34] and on the choice of the potential parameters [35]. Despite their individual limitations, AIMD and CMD simulations can be used in parallel to provide complementary information. Since DFT and classical model potentials are inherently diverse computational techniques, based on different mathematical formalisms, when AIMD and CMD results are consistent [26,27], it is reasonable to assume that the agreement is not accidental and that their predictions are realistic representations of actual physical phenomena.

Cubic TiN_x ($0.6 < x < 1.2$) structural, electronic, optical, and mechanical properties progressively depart from those of stoichiometric $B1$ TiN, with increasing concentrations of anion vacancies [15,36–38] and/or N self-interstitials [15,39,40] and Ti vacancies. In $\text{TiN}_{x<1}$, understoichiometry is primarily accommodated by means of N vacancies [41]. $\text{TiN}_{x<1}$ thin films are typically grown in reactive sputtering depositions at low N_2 partial pressures [36]. N self-interstitials are primarily incorporated in TiN layers at low deposition temperatures [42], which are required for electronic applications [43] and to coat heat-sensitive substrates [44].

Here, we use CMD simulations based on the modified embedded atom method (MEAM) [45] potential, which has been proven to reliably describe materials in various crystalline [34,46–48] and amorphous structures [49,50], validated by AIMD/DFT simulation results, to determine N self-interstitial (N^{I}) and N vacancy (N^{V}) migration pathways and diffusion coefficients in bulk $B1$ TiN. Titanium nitride, one of the first hard-coating materials [15,51,52], serves as a model to probe mass transport kinetics and mechanisms in NaCl structure TM nitride crystals in general. As a starting point in this study, we probe the mobility of N^{I} and N^{V} point-defects in the dilute limit, thus neglecting defect-defect interactions. In addition, our MD simulations reveal an unanticipated atomistic process for defect-free $B1$ TiN lattices, that is, the spontaneous formation of N self-interstitial/N vacancy ($\text{N}^{\text{I}}/\text{N}^{\text{V}}$) pairs, known as Frenkel pairs. Frenkel-pair formation/annihilation and dissociation rates are indicative of the thermal stability limit of bulk $B1$ TiN.

The rest of the paper is organized as follows. Section II A describes the computational details of CMD and AIMD simulations. Section II B describes the calculations of Frenkel-pair energetics and the simulations of Frenkel-pair dynamics. The methods used to calculate point-defect jump activation energies E_a , attempt frequencies A , and diffusion coefficients D are detailed in Sec. II C. Section III A briefly describes the MEAM mathematical formalism and the performances of our previous MEAM parameterization [35] in the representation of $B1$ TiN physical properties. Then, in Sec. III B, we motivate the need for a new set of TiN MEAM-parameters and the rationale followed to optimize these parameters. In Sec. III C, we demonstrate the validity of the present work TiN MEAM-parameterization by comparing the mobility of N point defects predicted by CMD/MEAM with that of AIMD simulations. The reliability of the new set of parameters is

also tested with respect to the representation of TiN_x ($\sim 0.7 < x \leq 1$) structural, elastic, and thermal properties. Section IV describes the dynamics of N self-interstitial (Sec. IV A) and vacancy migration (Sec. IV B), as well as of Frenkel-pair formation, annihilation, and dissociation (Sec. IV C) in bulk TiN. Corresponding diffusivities are provided. A discussion of the results and of their implications on mass transport in TiN follows in Sec. V. We summarize our findings in Sec. VI.

II. COMPUTATIONAL DETAILS

A. MD simulations

Ab initio molecular dynamics and CMD simulations are performed within the canonical ensemble NVT , integrating the equations of motion at 1-fs time intervals. The system is coupled with a Nosé thermostat using a Nosé mass of 40 fs; time period that allows for efficient equilibration [53] of energy and temperature fluctuations.

N interstitial and N vacancy jump rates are obtained as a function of temperature using TiN supercells comprised of $6 \times 6 \times 6$ $B1$ sites. The lateral size of the simulation cell is sufficient to avoid point-defect self-interactions. At each temperature T , the equilibrium Ti-N bulk interatomic distance $d_{\text{NN}}(T)$ is obtained, accounting for the experimental TiN average linear thermal expansion coefficient, $\sim 9 \times 10^{-6} \text{ K}^{-1}$ [54–56], by rescaling the 0 K d_{NN} value. This is necessary to avoid spurious strain effects on atomic jump rates [57]. In each MD run, prior counting diffusion events, the thermal oscillations are allowed to stabilize for 3 ps, a time interval sufficient to equilibrate the phonon modes of the system. The melting point of TiN is close to 3300 K [54]. This allows us to employ high simulation temperatures and thus obtain well-converged values of jump rates from MD. MD runs are stored in video files with a time resolution of 10 fs.

1. CMD simulations

Classical molecular dynamics simulations are carried out by describing the atomic interactions with the second-neighbor MEAM [45] potential as implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) [58].

Classical molecular dynamics N self-interstitial jump rates are estimated from ten statistically independent 10-ns runs performed at the temperatures $T = 1200, 1500$, and 1800 K , and ten statistically independent 1-ns runs at $T = 2000, 2200, 2500, 2700$, and 3000 K . For N vacancy diffusion, statistically independent CMD runs, with total durations of 4.0, 12.0, 3.8, 2.0, 0.6, 0.3, and $0.1 \mu\text{s}$, are carried out at $T = 1500, 1800, 2000, 2200, 2500, 2700$, and 3000 K , respectively.

2. AIMD simulations

The AIMD/DFT simulations are accomplished with the Vienna *Ab initio* Simulation Package (VASP) code [59] using the projector-augmented wave (PAW) [60] method and the Armiento-Mattsson functional (AM05) [61]. The AM05 was shown to provide an improved description of vacancy migration in bcc Mo [62] compared to the Perdew-Burke-Ernzerhof (PBE) 1996 generalized gradient approximation [63]. At each

AIMD time step, the total energy is evaluated to an accuracy of 10^{-5} eV/atom using a plane-wave energy cutoff of 400 eV. To assess the sensitivity of AIMD results with respect to the exchange and correlation functional used, we compare AIMD+AM05 N self-interstitial jump rates, obtained from preliminary ~ 0.15 -ns runs at 2500 and 2700 K, with those of AIMD simulations employing the local density approximation (LDA) and the PBE approximation. All preliminary test runs are performed by sampling the reciprocal space at the Γ point.

The AIMD+AM05 N self-interstitial jump rates are evaluated at the temperatures $T = 2200, 2500, 2700$, and 3000 K from ~ 0.18 -ns runs and at $T = 2000$ K from a longer simulation of ~ 0.39 ns. The Brillouin zone is integrated on $2 \times 2 \times 2$ k-point grids in the Monkhorst-Pack scheme [64]. Due to very low mobility of N vacancies compared to N self-interstitials, it is feasible to estimate N^V jump rates with AIMD only at very high simulation temperatures. Ten statistically independent AIMD+AM05 runs, for a total of 1-ns simulated time, are performed at $T = 3000$ K, integrating the Brillouin zone at the Γ point. The AIMD results are used to validate the predictions of the classical model potential.

B. Energetics and dynamics of Frenkel pairs

We calculate Frenkel-pair formation and dissociation energies for static stoichiometric TiN lattices by using MEAM and DFT. The DFT calculations are performed by using the AM05, PBE, and LDA functionals. The DFT energies are converged with respect to k-point grid thicknesses ($6 \times 6 \times 6$) and energy cutoff (500 eV) for the plane wave basis set. The 216-atom supercells are used for both DFT and MEAM calculations.

The Frenkel-pair formation energy is calculated as $E_{\text{form}}^F = E_{\text{Fp}} - E_{\text{bulk}}$, for which E_{Fp} is the energy of the Frenkel pair in its most stable 0-K configuration, and E_{bulk} is the energy of defect-free TiN. The Frenkel-pair dissociation energy is calculated as $E_{\text{diss}}^F = E_{\text{N}^I/\text{N}^V} - E_{\text{bulk}}$, for which $E_{\text{N}^I/\text{N}^V}$ is the energy of a TiN lattice containing one $\text{N}^I/\text{N}^{\text{lattice}}$ -pair (in its most stable orientation) and one N^V distant $2\sqrt{2}d_{\text{NN}}$ from the nitrogen self-interstitial.

Since Frenkel-pair formation events are rare on the time scales accessible to CMD, the simulation time necessary to observe these atomistic processes in AIMD runs might be unfeasibly long. Thus, to assess the degree of reliability of CMD Frenkel-pair formation rates k^F obtained in the temperature range 1500–3000 K, we estimate k^F via AIMD+AM05 runs performed at temperatures beyond the TiN melting point T_{melt} and compare the results with those of CMD simulations carried out at the same temperatures. To prevent melting, we fix the supercell volume $V^{T > T_{\text{melt}}}$ to an equilibrium volume slightly below the melting point ($V^{3200\text{K}}$). We run AIMD simulations at 4000, 4500, 4800, and 5000 K for approximately 0.22, 0.22, 0.10, and 0.03 ns, respectively, sampling the Brillouin zone Γ point. For comparison, 0.5-ns CMD runs are performed at the same temperatures.

C. Determination of diffusion parameters

Activation energies E_a and attempt frequencies A are obtained by linear interpolation of $\ln(k)$ vs $1/T$ data sets using

the Arrhenius equation:

$$\ln(k) = \ln(A) - \frac{E_a}{k_B} \left(\frac{1}{T} \right). \quad (1)$$

Jump rates k are recorded directly during MD runs. The uncertainties σ_k , σ_{σ_k} , σ_A , and σ_E associated with the values of k , $\ln(k)$, A , and E_a , respectively, are estimated following the methodology described in Ref. [26]. Assuming that nitrogen atoms consecutive hops are statistically independent, after a time t much larger than the inverse jump rate $1/k$ at a temperature T , the central limit theorem states that the probability p to find the point defect at a distance r from its origin is a normal distribution [65]

$$p(r, t) = \frac{1}{(4\pi D(T) t)^{3/2}} \exp\left(-\frac{r^2}{4D(T) t}\right). \quad (2)$$

The diffusion coefficient $D(T) = k(T) \cdot L^2/6$ is proportional to the jump rate k at the temperature T and to the square of the jump length L , which for N atoms diffusing in TiN between neighboring anion sites is equal to $\sqrt{2}d_{\text{NN}}(T)$. This allows for the evaluation of D at the simulated temperatures T_i via:

$$D(T_i) = k(T_i) \cdot d_{\text{NN}}^2(T_i)/3. \quad (3)$$

Uncertainties σ_D on diffusion coefficient values $D(T_i)$ are estimated from the expression $\sigma_D(T_i) = \sigma_k(T_i) \cdot d_{\text{NN}}^2(T_i)/3$. Thus, convolved activation energy E'_a and attempt frequency A' values, which are connected to point-defect isotropic/radial diffusion, and corresponding uncertainties σ'_E and σ'_A can be obtained from interpolation of the $\{D(T_i) \pm \sigma_D(T_i)\}$ data set. This leads to a general expression for the temperature-dependent diffusion coefficient:

$$D(T) \cdot \sigma'_D(T)^{\pm 1} = A' \cdot (\sigma'_A/\sqrt{2})^{\pm 1} \cdot \exp[-(E'_a \mp \sigma'_E/\sqrt{2})/(k_B T)]. \quad (4)$$

III. IMPROVED MEAM POTENTIAL PARAMETERIZATION FOR BULK TiN

A. MEAM formalism and performances of previous TiN MEAM parameter sets

Within the MEAM formalism, the total energy E_{tot} of a system is expressed as

$$E_{\text{tot}} = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} S_{ij} \phi_{ij}(R_{ij}) \right], \quad (5)$$

where F_i is the energy to embed atom i within the electron density $\bar{\rho}_i$, $\phi_{ij}(R_{ij})$ is the pair interaction of atoms i and j as a function of separation distance R_{ij} , and S_{ij} is a screening function [45].

Kim and Lee [47] were the first providing a MEAM parameterization for TiN compounds. This was shown to reproduce well fundamental bulk properties and to yield surface formation energies consistent with DFT calculation results. Subsequently, Kim's set of parameters was refined in order to improve the description of TiN surface properties that influence thin-film growth modes [35]. Beside returning bulk and surface properties consistent with DFT predictions

and experimental measurements [66–68], the TiN MEAM parameterization that was proposed previously [35] reproduces qualitatively and quantitatively well the AIMD/DFT diffusion behavior and diffusion kinetics of N and Ti monomers on TiN(001) terraces [26,27]. Nevertheless, it has also been shown that MEAM calculations employing such [35] a set of TiN parameters largely overestimate the strength of N adatom/N surface atom ($N_{\text{ad}}/N_{\text{surf}}$) bonds. This prevents migration of N adatoms on TiN(001) surfaces in CMD runs performed at all simulated temperatures [26].

B. Rationale for an improved MEAM description of TiN bulk properties

As predicted by DFT calculations [69] and confirmed in the present work AIMD runs, N self-interstitials incorporated in TiN find their most stable positions in split-bond configurations with N lattice atoms. This can be thought of as a N_2 dimer centered at a TiN anion lattice site. As for the case of N adatoms adsorbed on TiN(001) surfaces [26], also N self-interstitials in bulk TiN are closely located (N-N separation distance ~ 1 Å) to another nitrogen atom (N^I/N^{lattice} pair). Thus, the problem mentioned at the end of Sec. III A, i.e., MEAM overestimation of N-N bond strengths, is expected to translate in underestimated mobilities of N^I point defects.

In order to obtain reliable CMD N self-interstitial diffusion rates without altering the MEAM representation of the physical properties of bulk $B1$ TiN [35] in which the N-N equilibrium distance (~ 3 Å) is approximately three times larger than in a N_2 molecule or in a N^I/N^{lattice} pair, here, we modify one of the nitrogen MEAM parameters, namely, $\alpha(N, N)$, to reproduce DFT forces as a function of N-N separation distance in a N_2 molecule. Beside the N_2 formation energy and equilibrium bond length, which are taken from experiments, $\alpha(N, N)$ is the only MEAM parameter that controls the magnitude of the forces acting on N atoms in an isolated N_2 molecule. We stress that the N_2 molecule is here used as MEAM reference structure for nitrogen. For readers less familiar with the MEAM model potential, in the MEAM formalism the forces acting on an atom are obtained by relating the electron density in which the atom is embedded [$\bar{\rho}$; in Eq. (5)] to the electron density of the element reference structure. Thus, the more accurate is the quantification of the properties of element reference structures, the better will be the MEAM description of interatomic forces in a simulated material system. N-N DFT forces are estimated with both PBE and LDA. For these calculations, we use a simulation box of $10 \times 10 \times 10$ Å size, an energy cutoff of 500 eV, and Gaussian smearing with $\sigma = 0.1$ eV. Since PBE and LDA performances can be unsatisfactory for molecular systems [70], results are compared with those of calculations that partially account for exact electron-exchange energy.

The MEAM description of material properties is in general very sensitive to the set of parameters used [35,47]. Thus, the validity and applicability of the new parameterization for the investigation of TiN bulk properties in general is tested by comparing CMD/MEAM TiN_x ($\sim 0.7 < x \leq 1$) elastic constants, thermal expansion, and phonon dispersion with DFT [71–74] and experimental results [36,37,75–81].

Modified embedded atom method TiN phonon dispersion curves are calculated within the harmonic approximation

FIG. 1. (Color online) N-N interatomic forces as a function of N-N separation distance in N_2 , as obtained from *ab initio* and MEAM calculations using the original [47] (5.96) and the present paper's (4.33) $\alpha(N, N)$ MEAM parameter value. The enlarged view around the N_2 equilibrium bond length illustrates the results of hybrid functionals.

using the PHON code [82] for simulation boxes comprised of $12 \times 12 \times 12$ $B1$ TiN primitive unit cells. The supercells used to assess MEAM TiN_x ($x = 0.69, 0.79, 0.89$) properties are generated by stochastically selecting the anion vacancy positions on $6 \times 6 \times 6$ $B1$ lattice sites. Lattice parameters $a(x)$ are determined from the average TiN_x supercell equilibrium volume at the concentration x . C_{11} , C_{12} , and C_{44} TiN_x elastic constants, computed with MEAM following the procedure described in Ref. [83], are averaged over 500 values obtained for supercells with random vacancy arrangements. Shear moduli G and Young's moduli E are obtained from the elastic constant values applying the expression proposed by Hill [84]. The use of the Hill average allows for a meaningful comparison of the calculated moduli with those of indentation measurements conducted on polycrystalline or single-crystal thin film samples [36]. Poisson's ratios ν are estimated from the relationship $\nu = [1 - E/(3B)]/2$ [85]. The error bars on the values of elastic constants and moduli correspond to standard deviations. For comparison, DFT+AM05 TiN lattice parameters, elastic constants, and moduli are computed for 216-atom supercells on $6 \times 6 \times 6$ Monkhorst-Pack k-point grids, using a plane wave energy cutoff of 500 eV. TiN lattice parameters and bulk moduli are also calculated using the PBE and LDA functionals. The $B1$ TiN lattice parameter dependence on temperature is obtained by performing 0.1-ns CMD/MEAM runs by sampling the isothermal-isobaric NPT configurational space at $P = 0$ and $T = 300, 600, 900, 1200, 1500$, and 1700 K for $10 \times 10 \times 10$ atom supercells.

C. Optimization and validation of present work set of TiN MEAM-parameters

The DFT+LDA and DFT+PBE N-N interatomic forces obtained as a function of the N-N separation distance in a N_2 molecule are in mutual agreement (see Fig. 1). We tested whether accounting for partially exact electron-exchange energies would yield results significantly different to those of PBE and LDA functionals. Using the Gaussian code [86], we find that progressively increasing the degree of exact

exchange (from 0 to 50%), by using the Becke-Lee-Yang-Parr (BLYP), B3LYP, B1LYP, and the Becke-Half-and-Half-LYP (BHandHLYP) hybrid functionals [87], returns essentially the same results as the PBE and LDA approximations. The LDA estimation of the N_2 equilibrium bond length, 1.103 Å, compares very well with the experimental value of 1.098 Å. DFT+PBE predicts a slightly higher value of 1.114 Å. The BLYP, B3LYP, B1LYP, and BHandHLYP functionals yield N_2 equilibrium bond lengths of 1.117, 1.105, 1.103, and 1.091 Å, respectively. The use of the original $\alpha(N, N)$ parameter value, 5.96, leads to MEAM N-N interatomic forces largely different to those determined by DFT calculations (see Fig. 1). Setting $\alpha = 4.33$, instead, yields MEAM N-N forces matching the *ab initio* results.

As detailed in the following section, CMD runs employing $\alpha(N, N) = 5.96$ yield N self-interstitial jump rates k^I , which are almost two orders of magnitude smaller than AIMD k^I values at all simulated temperatures. In contrast, the use of a modified α parameter, $\alpha(N, N) = 4.33$, leads to k^I values close the uncertainty range of AIMD results. It should be noted that the use of $\alpha(N, N) = 4.33$ is not expected to produce significant changes in TiN surface mass transport properties in comparison to our previous CMD predictions based on $\alpha(N, N) = 5.96$, as N-N interatomic distances for most of the phenomena studied in Refs. [27,35,88] were ~ 3 Å.

To assure the validity of the new parameterization for the investigation of TiN bulk properties in general, we compare CMD/MEAM TiN_x ($\sim 0.7 < x \leq 1$) elastic constants, thermal expansion, and phonon dispersion results with those of DFT calculations [71–74] and experimental measurements [36,37,75–81].

Figure 2 illustrates the phonon dispersion curves of B1 TiN obtained from 0-K MEAM calculations in comparison with experiments [76] and DFT [71] results. Overall, MEAM results are in good agreement with inelastic neutron scattering measurements [see Fig. 2(a)] and previous DFT calculations [see Fig. 2(b)]. Due to the use of screening [89], our classical model potential cannot reproduce the phonon softening (Kohn anomalies) observed in DFT and experimental acoustic branches on the $\Gamma \rightarrow X$ and $K \rightarrow \Gamma$ directions, and at the L point, as this stems from long-range atomic interactions. The largest discrepancy between experimental and theoretical results is visible on the $\Gamma \rightarrow L$ direction, for which MEAM and DFT (as will be seen in Fig. 4 in Ref. [71] for direct comparison between DFT results and experiments) reproduce well only the optical and acoustic phonon frequencies, respectively. On the $\Gamma \rightarrow X$ direction, both the MEAM and DFT optical mode predictions differ from neutron scattering measurements. The experiments, however, were performed at room temperature and for slightly understoichiometric samples ($TiN_{0.98}$); this might explain the mismatch with the theoretical results, obtained at 0 K for defect-free TiN.

The TiN lattice parameter variation Δa dependence on temperature is calculated from CMD/MEAM and compared with experimental findings [75]. The experimental and theoretical Δa results match quite well up to 1200 K, while slightly deviate at higher temperatures because the experimental Δa vs T trend is not as linear as the CMD one. The too linear CMD Δa trend might be due to neglected vibrational entropies for the estimation of stresses in the LAMMPS code. From the

FIG. 2. (Color online) B1 TiN phonon dispersion as calculated in the present work from MEAM using a $\alpha(N, N)$ value of 4.33 in comparison with (a) neutron scattering measurements [76] and (b) DFT [71] results. MEAM results are solid red lines. DFT results are dotted black lines. Open squares and filled circles indicate experimental longitudinal and transversal phonon frequencies, respectively.

CMD Δa vs T curve, we obtain a linear thermal expansion coefficient of $(8.4 \pm 0.2) \times 10^{-6} K^{-1}$, in good agreement with the experimental results $8.5\text{--}9.5 \times 10^{-6} K^{-1}$ [54–56].

Figure 3 illustrates the TiN_x lattice parameter a , elastic constants C_{11} , C_{12} , and C_{44} , elastic moduli B , G , and E , and Poisson's ratio ν dependences on the nitrogen concentration x as calculated by MEAM and DFT [72,73,74] and as determined experimentally [36,37,76–81]. The TiN MEAM lattice parameter a decreases monotonically with the N composition from 4.242 Å for $x = 1$ ($d_{NN} = 2.121$ Å is one of TiN MEAM-parameters) to ~ 4.21 Å for $x \sim 0.7$, in excellent agreement (maximum discrepancy of $\sim 0.3\%$) with experiments conducted on TiN_x thin films [[36]; see Fig. 3(a)]. The present work DFT estimations [not included in Fig. 3(a)] of stoichiometric TiN lattice constants vary by up to $\sim 2\%$, depending on the exchange-correlation approximation used. The DFT+AM05 calculations return $a = 4.220$ Å, between the PBE ($a = 4.256$ Å) and the LDA ($a = 4.188$ Å) values. The generalized gradient approximation of Perdew and Wang (PW91) returns essentially the same result of PBE ($a = 4.254$ Å) [72]. Thus, the AM05, PBE, and PW91 functionals yield TiN lattice parameters equally close to the 300 K experimental value ($a = 4.24$ Å) [36], with an error lower than 1%.

FIG. 3. (Color online) TiN_x lattice parameters and elastic properties calculated with MEAM (using a MEAM-parameter $\alpha(N, N) = 4.33$) as a function of the N concentration x ($0.6 < x \leq 1$) in comparison with experimental measurements. TiN_x bulk and thin-film elastic constants and moduli determined experimentally: sound velocities by T. Lee *et al.* [36], neutron scattering by Kress *et al.* [76], sound velocities by Y. C. Lee *et al.* [79], sound velocities by Kral *et al.* [77] and Wolf [78], synchrotron x-ray diffraction by Shebanova *et al.* [81], Brillouin scattering and nanoindentation by Jiang *et al.* [80], and nanoindentation by Shin *et al.* [37]. *Ab initio* results are taken from previous DFT+PW91 calculations [72], DFT+PW91 by Ashley *et al.* [73], DFT+LDA by Jhi *et al.* [74], and DFT+AM05/PBE/LDA (present paper).

FIG. 4. (Color online) Diffusion of N self-interstitials in B1 TiN as predicted by AIMD simulations performed at (a) 2000 K and (b), (c), and (d) 3000 K. N^I migrates from one anion site to another by passing through metastable eightfold-coordinated tetrahedral sites (orange dots) located at the center of B1 conventional unit cells. N^I diffusion pathways are marked by double-colored solid lines. Black dotted lines evidence the motion of N lattice atoms during N^I migration from one split-bond configuration to another. Gray (blue) balls indicate the equilibrium position of Ti (N) lattice atoms. Atom and diffusion pathway projections onto (100), (010), and (001) box side planes facilitate the visualization of N^I migration trajectories. Each panel represents the dynamics of atoms for a total duration of ~ 0.7 ps.

Acoustic wave velocity measurements were used to assess TiN elastic constants [36,77–79]. These are $C_{11} = 605\text{--}649$ GPa, $C_{12} = 145\text{--}165$ GPa, and $C_{44} = 156\text{--}171$ GPa [see Figs. 3(b)–3(d)]. The DFT + AM05 calculations overestimate C_{11} (714 GPa) and underestimate C_{12} (125 GPa) values compared to the experimental ranges. The DFT+PW91 calculations yield a C_{11} value (640 GPa) within the experimental range, while underestimate C_{12} (115 GPa) [72]. Both AM05 and PW91 C_{44} results (169 and 159 GPa, respectively) are within the experimental range.

Due to the modification of the $\alpha(N, N)$ parameter, MEAM TiN C_{11} and C_{44} elastic constants decrease from 671 and 170 (see Ref. [35]) to 608 and 147 GPa, respectively. The reduction of the C_{11} value is accompanied by an increase in C_{12} , from 107 to 138 GPa. The new MEAM C_{11} and C_{12} values (608 and 138 GPa) are in closer agreement with those determined experimentally than our previous [35] MEAM estimations based on $\alpha(N, N) = 5.96$. The present work MEAM C_{44} value (147 GPa) is slightly below the experimental range [see Fig. 3(d)].

Our DFT AM05, PBE, and LDA calculations return TiN bulk moduli of 321, 305, and 350 GPa, respectively [see Fig. 3(e)]. Previous DFT+PW91 calculations [72,73] reported

B values of 279 and 290 GPa. The AM05 and PBE B values are within the experimental range ($\sim 300\text{--}325$ GPa) [79]. Overall, both the AM05 and the PBE approximations produce lattice constants and bulk moduli in close agreement with experiments. The bulk modulus is one of the MEAM parameters ($\alpha(\text{Ti}, N) \propto \sqrt{B}$). For convenience, we choose to use the same B MEAM parameter value (295 GPa) as in Ref. [35].

In agreement with the experimental and DFT trends, $\text{TiN}_{x<1}$ properties estimated using the modified set of MEAM parameters vary monotonically with x . With the exception of the Poisson's ratio ν , which increases, all $\text{TiN}_{x<1}$ elastic constants and moduli decrease with x . Overall, MEAM results are in good quantitative agreement with experimental and DFT values. This assures that the MEAM description of interatomic forces in understoichiometric $\text{TiN}_{x<1}$ is accurate and validates

TABLE I. List of LAMMPS/MEAM parameters used in the present work. See Refs. [47,48,95] for a detailed description of the MEAM formalism and clarification of the meaning of each LAMMPS/MEAM parameter.

LAMMPS/MEAM parameter	Pair interaction		
	N-N	Ti-Ti	Ti-N
Reference structure	dimer	hcp	cubic-B1
E_c (eV/atom)	4.880	4.870	6.615
d_{NN} (Å)	1.100	2.920	2.121
α	4.3300	4.7294	4.8848
A	1.73	0.66	–
$\beta^{(0)}$	2.74	2.70	–
$\beta^{(1)}$	4.00	1.00	–
$\beta^{(2)}$	4.30	3.00	–
$\beta^{(3)}$	4.00	1.00	–
$t^{(0)}$	1.00	1.00	–
$t^{(1)}$	0.10	6.80	–
$t^{(2)}$	1.20	– 2.00	–
$t^{(3)}$	0.50	– 12.00	–
ρ_0	18	1	–
ibar (Γ func. form)	3	3	–
$C_{\min}$	2.00	1.00	–
$C_{\max}$	2.80	1.44	–
Second nearest neighbor	0	1	1
Attraction	0	0	0
Repulsion	0	0	0
ZBL	1	1	1
$C_{\min}[(\text{Ti-Ti})/\text{N}]$	–	–	0.01
$C_{\min}[(\text{N-N})/\text{Ti}]$	–	–	0.09
$C_{\min}[(\text{Ti-N})/\text{N}]$	–	–	1.46
$C_{\min}[(\text{Ti-N})/\text{Ti}]$	–	–	0.81
$C_{\max}[(\text{Ti-Ti})/\text{N}]$	–	–	2.80
$C_{\max}[(\text{N-N})/\text{Ti}]$	–	–	2.93
$C_{\max}[(\text{Ti-N})/\text{N}]$	–	–	2.80
$C_{\max}[(\text{Ti-N})/\text{Ti}]$	–	–	1.44
r_{cutoff} (Å)	–	–	5.3
Δr (Å)	–	–	0.3
Mixture reference $t^{(i)}$	–	–	0
ialloy	–	–	0
$E_{\text{Rose form}}$	–	–	0
$t^{(1)}$ augmentation	–	–	0
Background density	–	–	0
Embedding negative	–	–	0

the use of the present work MEAM parameterization for the estimation of N vacancy diffusion coefficients. The full set of TiN LAMMPS/MEAM parameters [35,48] used in this paper is listed in Table I.

Finally, we note that the use of the previous set of MEAM parameters [35] returns (results not shown) TiN_x structural, thermal, and elastic properties similar to the MEAM predictions reported here.

IV. RESULTS

A. Nitrogen self-interstitial diffusion

During sputtering deposition, the incorporation of N atoms in TiN interstitial positions is favored by nonequilibrium conditions, such as low temperatures and energetic particle bombardement [15,39]. In TiN_{x>1}, overstoichiometry accommodated by N self-interstitials produces internal stresses that lead to an increase in TiN lattice parameter compared to the defect-free rocksalt structure. CMD and AIMD simulations confirm that N self-interstitial stable positions in bulk TiN are in pairs formed with the N lattice atom, known as N₂ split-bond configurations [69]. At all simulated temperatures, the N₂ dimer rotates and vibrates, with no clear preferential N-N bond axis orientation, while maintaining its center of mass close to an anion sublattice site. Eventually, when the dimer bond breaks, one of the N₂ nitrogen atoms moves to a metastable tetrahedral position [19], surrounded by four Ti and four N atoms (see Fig. 4), while the other remains at the same lattice site. Finally, the N point defect located in the eightfold position migrates to one of the neighboring (including the former) anion sites, thus reforming a N₂ dimer. We note that diffusion events in which N self-interstitials return from a tetrahedral position to the original site are not counted in our MD jump-rate results.

Preliminary AIMD test runs performed by employing the AM05, LDA, and PBE approximations, and integrating the Brillouin zone at the Γ point, return similar jump rates k^I for migration of N self-interstitial atoms (see Table II). This indicates that AIMD k^I values are not significantly dependent on the choice of the exchange-correlation functional. Considering the difference in PBE and LDA N₂ molecule equilibrium bond lengths (see Fig. 1), it is also reasonable to assume that slightly modifying the $d_{NN}(\text{N}, \text{N})$ MEAM-parameter value (1.1 Å) used in this paper would not produce significant variations on the estimated CMD k^I values. Increasing the k-point grid thickness up to $2 \times 2 \times 2$ in AIMD+AM05 runs produces relatively small variations in k^I compared to the Γ -point

FIG. 5. (Color online) AIMD and CMD N self-interstitial jump rates $\ln[k^I]$ vs inverse temperature $1/T$. CMD runs performed using a MEAM parameter $\alpha(\text{N}, \text{N}) = 4.33$ return jump rates close to the AIMD values. Error bars correspond to uncertainties σ_k (see text). $T_{\text{melt}} \sim 3250$ K is the melting point of TiN.

sampling. This lends confidence that the AIMD N-vacancy jump rate k^V value, obtained by sampling the reciprocal space only at the Γ point (see below), is reliable.

The CMD k^I results determined by using the original [35] $\alpha(\text{N}, \text{N})$ MEAM-parameter value (5.96) are almost two orders of magnitude smaller than those of AIMD simulations (see Table II). This confirms (as suggested in Sec. III B) that k^I is very sensitive to the magnitude of short-range N-N interatomic forces. The presently modified value of α (4.33) produces CMD N self-interstitial jump rates close to the uncertainty range of AIMD results (see Fig. 5 and Table II). The differences between CMD ($\alpha = 4.33$) and AIMD jump rates are small compared to the overall accuracy of CMD and AIMD simulation results. Even first-principle AIMD/DFT predictions (quantitatively more reliable than those of classical potential models) are affected by exchange-correlation errors, limited k-point grid thicknesses, and short simulation times (not well converged jump rates). For instance, we note that 2700-K AIMD+PBE k^I results are two times larger than those of AIMD+AM05 simulations (Γ -point sampling). From linear interpolation of the CMD $\ln(k^I)$ vs $1/T$ data set [Eq. (1)], we extract N^I diffusion activation energies $E_a^I = (1.17 \pm 0.13)$ eV and attempt frequencies $A^I = 0.45 (\times 1.9^{\pm 1}) \times 10^{13} \text{ s}^{-1}$. The $\ln(k^I)$ dependence on the

TABLE II. AIMD N self-interstitial jump rate k^I dependence on exchange and correlation functional and k-point mesh thickness in comparison with k^I obtained from CMD runs employing the previous (5.96) and present (4.33) $\alpha(\text{N}, \text{N})$ MEAM-parameter value.

T (K)	$k^I (10^{10} \text{ s}^{-1})$					
	AIMD				CMD	
	Γ point		$2 \times 2 \times 2$ k-point grid		$\alpha = 4.33$	$\alpha = 5.96$
	LDA	PBE	AM05	AM05		
2700	8.3 ± 2.4	10.2 ± 1.1	5.3 ± 1.5	7.5 ± 1.1	3.09 ± 0.08	0.16 ± 0.01
2500	4.6 ± 1.8	3.4 ± 1.0	4.4 ± 1.8	4.9 ± 1.1	2.07 ± 0.08	0.08 ± 0.01

inverse temperature is linear (Arrhenius behavior) on the entire simulated temperature range (1200–3000 K). AIMD+AM05 $\ln(k^I)$ vs $1/T$ trends correspond to $E_a^I = (1.46 \pm 0.37)$ eV and $A^I = 3.94 (\times 4.5^{\pm 1}) \times 10^{13} \text{ s}^{-1}$. The AIMD σ_{A^I} and $\sigma_{E_a^I}$ uncertainties are large compared to the estimated A^I and E_a^I values due to a relatively low number of diffusion events recorded during AIMD simulations.

E_a^I and A^I results obtained from AIMD and CMD simulations are mutually consistent. present paper E_a^I values compare well with those determined via 0-K DFT+GGA calculations [19], $E_a = 1.28$ eV, and experimental measurements by Elstner *et al.*, $E_a = 1.23 \pm 0.07$ eV [42]. This indicates that experimental N self-diffusion activation energies ranging between 2–2.5 eV (see Refs. [16,17,90,91]) are not likely to derive from diffusion of isolated N self-interstitials, as was suggested [91]. Based on DFT calculation results, Tsetseris *et al.* [19] concluded that E_a values close to 2.2 eV are to be attributed to diffusion of N^I/N^I -pairs. On the other hand, Perry [92] inferred that $E_a \sim 2.1$ eV is due to N vacancies migrating toward N self-interstitials and not vice versa. The latter hypothesis, however, seems unrealistic considering that N vacancy diffusion in most TM nitride systems requires activation energies ≥ 3 eV [14].

It should be stressed that the good agreement between our MD estimations of E_a and the experimental result of Elstner *et al.* [42], $E_a \sim 1.2$ eV, could be accidental. In that experiment, as-deposited TiN films exhibited lattice parameters ranging between 4.26–4.27 Å; ~ 0.5 – 0.7% larger than the lattice constant of stoichiometric B1 TiN ($a = 4.24$ Å). This means that the concentration of N self-interstitials in the experiments of Elstner *et al.* might be higher than the one used for the present paper's simulations ($\sim 1\%$ of the total number of N atoms). According to DFT calculation results, when closely located, N self-interstitials form N^I/N^I pairs that diffuse with an activation energy higher than 2 eV [19].

Recently, it has been shown that assuming fully uncorrelated jump probabilities $P \propto A \cdot \exp(-E_a)$ (random walk) of Ti adatoms on TiN(001) yields slightly inaccurate surface diffusion coefficients [27]. In the present paper's MD runs performed at $T \geq 2500$ K, we occasionally observe N self-interstitial double jumps, i.e., two single jumps occurring along the same direction within a short time interval (much smaller than the average inverse jump rate $1/k$). In this paper, however, we neglect the effect of highly correlated jumps on diffusion coefficients due to an insufficient statistics for these events. Thus, each double jump is counted as two uncorrelated single jumps. The CMD and AIMD k^I values are in good agreement at all simulated temperatures. We estimate [Eqs. (3) and (4)] that the temperature-dependent diffusion coefficient of noninteracting N self-interstitials $D^I(T)$ has an exponential prefactor $A^I = 7.28 (\times 1.8^{\pm 1}) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and an activation energy $E_a^I = (1.17 \pm 0.13)$ eV (CMD results) and $A^I = 6.35 (\times 2.7^{\pm 1}) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ and $E_a^I = (1.47 \pm 0.23)$ eV (AIMD results; see Fig. 6). We stress that in Fig. 6 (see extrapolated D^I values), we assume that the real $\ln(D^I)$ vs $1/T$ curve maintains a linear trend even at temperatures lower than 1200 K (lowest simulated MD temperature). This is reasonable considering the close agreement between the present paper's E_a^I values and the 0-K DFT estimation [19].

FIG. 6. (Color online) AIMD and CMD N self-interstitial diffusion coefficient D^I dependence on temperature. Shaded regions correspond to uncertainty ranges σ'_D estimated as described in Eq. (4).

B. Nitrogen vacancy diffusion

Due to the high energy of formation of Ti point defects in interstitial or antisite positions, understoichiometry in $\text{TiN}_{x<1}$ is basically exclusively accommodated by means of N vacancies [15]. Various experimental studies reported activation energies for nitrogen self-diffusion in TiN close to 2.2 eV [14]. These E_a values were generally attributed to diffusion of nitrogen vacancies. Another experimental paper indicated that N^V migration in B1 TiN requires a much higher activation energy $E_a^V = 3.9$ eV [16]. This value was speculated to be incorrect due to uncertainty regarding the crystal structure of the TiN samples employed for the experiments [16]. Nevertheless, carbon and nitrogen self-diffusion occurs with activation energies higher than 3 eV in many cubic TM carbide and nitride systems [14]. Moreover, previous DFT investigations found $E_a^V \simeq 4$ eV for both TiN and ZrN [19].

The AIMD simulations performed at 3000 K show that N^V migrate between neighboring TiN anion sublattice sites via $\langle 110 \rangle$ translations, in agreement with 0-K DFT calculations [19]. Each of these events entails that one of the 12 neighbor nitrogen lattice atoms moves into the vacancy site (see Fig. 7). Nitrogen vacancy jump rates k^V assessed by AIMD runs at 3000 K are $\sim 3 \times 10^9 \text{ s}^{-1}$, that is, three N^V diffusion events are recorded during a simulated time of 1 ns. Due to insufficient statistics of recorded N^V diffusion events, the uncertainty σ_{k^V} is large (see AIMD error bar in Fig. 8) in comparison with the magnitude of the estimated AIMD k^V value. The latter, however, closely matches with the k^V value obtained from CMD runs at the same temperature ($k^V = 2.37 \times 10^9 \text{ s}^{-1}$). This lends confidence that all CMD/MEAM k^V values reported here are reliable.

Figure 8 is a plot of the CMD N vacancy jump rate $\ln(k^V)$ vs the inverse temperature $1/T$. No N^V migration event was observed during 4- μs CMD runs performed at 1500 K, indicating that $k^V < 2.5 \times 10^5 \text{ s}^{-1}$ at this temperature. From linear interpolation of the $\{\ln[k^V(T_i)] \pm \sigma_{k^V}(T_i)\}$ data set ($T_i = 1800, 2000, 2200, 2500, 2700$, and 3000 K), we obtain a

FIG. 7. (Color online) Diffusion of N vacancies in *B1* TiN as predicted by AIMD simulations performed at 3000 K. A nitrogen lattice atom migrates from its bulk position into a neighboring vacant anion site by moving along the [101] direction. The N^{lattice} diffusion pathway is marked by a double-colored solid line. Gray (blue) balls indicate the equilibrium position of Ti (N) lattice atoms. Atom and diffusion pathway projections onto (100), (010), and (001) box side planes facilitate the visualization of the N^{lattice} migration trajectory to the vacancy site. The figure represents the dynamics of atoms for a total duration of ~ 1 ps.

CMD N^{V} jump probability $P^{\text{V}}(T)$, with attempt frequency $A^{\text{V}} = 267(\times 2.6^{\pm 1}) \times 10^{13} \text{ s}^{-1}$ and activation energy $E_a^{\text{V}} = (3.65 \pm 0.23) \text{ eV}$. The vacancy diffusion activation energy value determined from CMD is consistent with the 0-K DFT estimation ($E_a^{\text{V}} = 3.8 \text{ eV}$) [19]. The good agreement between classical and *ab initio* results supports the hypothesis

FIG. 8. (Color online) AIMD and CMD N vacancy jump rates $\ln[k^{\text{V}}]$ vs inverse temperature $1/T$. Error bars correspond to uncertainties σ_k (see text).

that the experimental E_a value of 3.9 eV [16] derives from measurements of N^{V} diffusion in *B1* TiN. It should be stressed, however, that our MD results are obtained within a simulation temperature interval (1800–3000 K), which overlaps only partially with the temperature range used in the experiments described in Ref. [16] (1650–2000 K). Anharmonic lattice vibrations, progressively more relevant for increasing temperatures, could produce slope variations in $\ln(k^{\text{V}})$ vs $1/T$ curves [30] corresponding to a change in activation energy with temperature, in agreement with Matzke's assessment on nonlinear diffusivities in TM nitrides [12]. This effect was also reported for diffusion of ^{15}N isotopes in $\text{TiN}_{0.94}$ polycrystals [17]. From CMD $k^{\text{V}}(T_i)$ results, we extract a temperature-dependent N^{V} diffusion coefficient $D^{\text{V}}(T)$ with exponential prefactor $A' = 3.89(\times 2.5^{\pm 1}) \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$ and activation energy $E_a' = (3.65 \pm 0.23) \text{ eV}$.

C. Frenkel-pair formation, annihilation, and dissociation in defect-free TiN

1. CMD prediction

In addition to providing the first theoretical estimate of nitrogen point-defect diffusion coefficients in TiN, the present paper's CMD simulations predict an unanticipated atomistic process, which controls the formation of N-self-interstitial/N-vacancy point-defect pairs (Frenkel pairs) in defect-free TiN. This entails that a nitrogen lattice atom leaves its anion site and bonds to a neighboring nitrogen lattice atom [see Figs. 9(a) and 9(b)]. In Fig. 9(b), the Frenkel pair is shown in its most stable 0-K configuration (see Sec. IV C 2). However, at all simulated MD temperatures ($T \geq 1500 \text{ K}$), the N_2 ($N^{\text{I}}/N^{\text{lattice}}$ pair) dimer rotates and vibrates, with no distinctly favored bond axis orientation. Although the formation of Frenkel pairs is relatively frequent at all simulated temperatures in CMD runs, due to the complex dynamics of $N^{\text{I}}/N^{\text{V}}$ -pairs, it is difficult to determine k^{F} accurately. Therefore, we arbitrarily set $\sigma_{k^{\text{F}}}(T_i) = \pm k^{\text{F}}(T_i)/2$. Estimated CMD Frenkel-pair formation activation energies E_a^{F} and attempt frequencies A^{F} are $(1.82 \pm 0.30) \text{ eV}$ and $0.0015(\times 5^{\pm 1}) \times 10^{13} \text{ s}^{-1} \text{ atom}^{-1}$, respectively (see Fig. 10).

In most cases, Frenkel-pair lifetimes are shorter than 1 ns; the newly formed self-interstitial N_2 dimer dissociates and one of the nitrogen atoms migrates into the vacant anion position [see Figs. 9(c)–9(f)]. To a good approximation, 50% of these events result in the exchange of two nitrogen lattice atoms ($\text{N}-N^{\text{Exc}}$) [see Figs. 9(e) and 9(f)]. This stems from an equal probability for the nitrogen atoms forming the $N^{\text{I}}/N^{\text{lattice}}$ dimer [see Figs. 9(c) and 9(e)] to migrate to the vacancy site. Thus, activation energies and attempt frequencies of $\text{N}-N^{\text{Exc}}$ events are $E_a^{\text{Exc}} = E_a^{\text{F}}$ and $A^{\text{Exc}} = A^{\text{F}}/2$. The exchange of indistinguishable particles does not produce net mass transport fluxes. Considering, however, the exchange of different nitrogen isotopes, $\text{N}-N^{\text{Exc}}$ events yield a net mass transfer with a corresponding diffusion coefficient per atom $D^{\text{Exc}}(T)$ with $A' = 1.25(\times 5^{\pm 1}) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ atom}^{-1}$ and $E_a' = (1.83 \pm 0.30) \text{ eV}$.

Occasionally, Frenkel-pair N self-interstitials dissociate from the vacancy site by diffusion [see Figs. 9(g) and 9(h)]. The $N^{\text{I}}/N^{\text{V}}$ -pair interaction weakens as the $N^{\text{I}}/N^{\text{V}}$ separation

FIG. 9. (Color online) Schematic representation of Frenkel-pair formation, annihilation, and dissociation. Spontaneous formation of Frenkel pairs in defect-free $B1$ TiN: (a) and (b) a nitrogen lattice atom moves to a neighbor anion site thus forming a N^I/N^V pair. Frenkel pairs are shown in their most stable 0-K configuration: the N^I/N^{lattice} pair bond axis is oriented along a $\langle 110 \rangle$ direction with the two nitrogen (N^I/N^{lattice}) atoms equally distant from the vacancy site N^V . Frenkel-pair annihilation mechanisms: (c) and (d) the nitrogen lattice atom returns to its initial position; (e) and (f) two nitrogen lattice atoms exchange position in comparison with the original configuration seen in (a). Frenkel-pair dissociation: (g) and (h) one of the two nitrogen atoms forming the N_2 split-bond configuration diffuses to an anion site further away from N^V .

distance increases. When the latter is much larger than d_{NN} , diffusion of the N^I and that of the N^V become mutually

uncorrelated. From Frenkel-pair formation and dissociation rates, in principle, one could estimate the equilibrium concentration of N^I and N^V in stoichiometric TiN. However, the Frenkel-pair dissociation rate cannot be evaluated with reasonable accuracy due to scarce statistics for these events.

FIG. 10. (Color online) CMD Frenkel-pair formation rates $\ln[k^F]$ vs inverse temperature $1/T$. Error bars correspond to uncertainties $\sigma_k = \pm k^F(T)/2$ (see text). CMD $N-N^{\text{Exc}}$ rates are approximately equal to $k^F(T)/2$. The inset shows AIMD and CMD results at $T > T_{\text{melt}}$.

2. DFT/AIMD verification of MEAM/CMD Frenkel-pair energetics and dynamics

As described in Sec. III, our classical model potential has been initially optimized in order to reproduce N^I AIMD diffusion rates. The spontaneous formation of Frenkel pairs, as well as their annihilation and dissociation, is an unexpected outcome of our CMD simulations aiming to model diffusion of N^I and N^V in TiN. Based on the CMD k^F value obtained at 3000 K ($k^F \sim 2.5 \times 10^7 \text{ s}^{-1} \text{ atom}^{-1}$), approximately three Frenkel-pair formation events should occur during 1.2-ns AIMD runs performed at the same temperature. However, no Frenkel-pair formation was recorded in AIMD simulations at 3000 K. Thus, it is necessary to verify the reliability of the CMD predictions regarding Frenkel-pair energetics and dynamics.

Table III lists Frenkel-pair formation E_{form}^F and dissociation E_{diss}^F energies obtained by MEAM and DFT calculations. At 0 K, Frenkel-pair most stable configurations are with the N^I/N^{lattice} pair bond axis oriented along a $\langle 110 \rangle$ direction and

TABLE III. The 0-K Frenkel-pair formation and dissociation energies as estimated by MEAM and DFT.

Frenkel-pair energies (0 K)	MEAM	DFT		
		AM05	PBE	LDA
$E_{\text{form}}^{\text{F}}$ (eV)	3.3	7.2	7.1	8.1
$E_{\text{diss}}^{\text{F}}$ (eV)	3.1	7.0	6.9	7.8

the two nitrogen ($\text{N}^{\text{I}}/\text{N}^{\text{lattice}}$) atoms equally distant from the vacancy site N^{V} [see Fig. 9(b)]. DFT+AM05 and DFT+PBE $E_{\text{form}}^{\text{F}}$ results are very similar ($E_{\text{form}}^{\text{F}} \sim 7$ eV), while $E_{\text{form}}^{\text{F}}$ estimated by DFT+LDA is slightly higher ($E_{\text{form}}^{\text{F}} \sim 8$ eV). The DFT+PBE $E_{\text{form}}^{\text{F}}$ value is essentially equal to $E_{\text{form}}^{\text{I}} + E_{\text{form}}^{\text{V}} = 4.60 + 2.41$ eV obtained in previous DFT investigations [69]. The MEAM predicts an $E_{\text{form}}^{\text{F}}$ value of 3.3 eV, considerably smaller than all DFT results. The MEAM $E_{\text{form}}^{\text{V}}$ and $E_{\text{form}}^{\text{I}}$ values, referenced to the 0-K energy of a N_2 gas molecule ($= 2 \times 4.88$ eV; see Table I), are 2.0 and 1.1 eV, respectively. Thus, while MEAM and DFT $E_{\text{form}}^{\text{V}}$ results are in good agreement, the MEAM-potential large underestimation of N self-interstitial formation energies translates also in too small $E_{\text{form}}^{\text{F}}$. We note that MEAM parameterized with the previous $\alpha(\text{N}, \text{N})$ value ($\alpha = 5.96$) would return $E_{\text{form}}^{\text{I}} = 1.2$ eV, essentially the same result of MEAM + $[\alpha(\text{N}, \text{N}) = 4.33]$, and $E_{\text{form}}^{\text{V}} = 1.7$ eV, in worse agreement with DFT than the MEAM value of the present paper.

The large discrepancy between MEAM and DFT $E_{\text{form}}^{\text{I}}$ results reveals a limited predictive capability of the classical model for the evaluation of 0-K N self-interstitial energetics. Despite this, the present paper's MEAM parameterization yields N^{I} dynamics in very good agreement with *ab initio* simulations (see Sec. IV A). Nevertheless, the quantitative validity of CMD Frenkel-pair formation rates k^{F} is to be verified. The large difference between DFT and MEAM $E_{\text{form}}^{\text{F}}$ values indicates that AIMD Frenkel-pair formation rates k^{F} could be much lower than those determined via CMD.

To qualitatively assess the difference between AIMD and CMD k^{F} rates, we perform AIMD test runs at simulation temperatures beyond the TiN melting point (choice due to the very low occurrence probability of Frenkel-pair formation), and compare the results to those of CMD simulations carried out at the same temperatures. We note that, in all MD runs,

the atoms maintain their average vibrational position close to ideal B1 lattice sites for the entire duration of the simulation. This ensures that melting is prevented, at least on the simulated time scales, upon fixing the supercell volume to an equilibrium volume below T_{melt} .

The AIMD Frenkel-pair formation rates recorded at $T > T_{\text{melt}}$ are much smaller than those obtained by CMD (see inset in Fig. 10). We find that $k^{\text{F}}(\text{AIMD}) \simeq k^{\text{F}}(\text{CMD})/10$ at 5000 K, and $k^{\text{F}}(\text{AIMD}) \simeq k^{\text{F}}(\text{CMD})/60$ at 4000 K. CMD and AIMD k^{F} values at $T_{\text{melt}} \sim 3300$ K, extrapolated by the $\ln[k^{\text{F}}]$ vs $1/T$ data at $T > T_{\text{melt}}$, yield $k^{\text{F}}(\text{AIMD}) \simeq k^{\text{F}}(\text{CMD})/300$. The evaluation of k^{F} at temperatures below the TiN melting point directly via AIMD simulations is beyond the scope of this paper.

Despite the fact that k^{F} values obtained via CMD at $T < T_{\text{melt}}$ are likely to be largely overestimated, it is important to note that AIMD simulations at $T > T_{\text{melt}}$ validate all reaction pathways, including Frenkel-pair spontaneous formation, annihilation/ $\text{N}-\text{N}^{\text{Exc}}$, and dissociation, observed in CMD runs. We conclude that the dynamics of Frenkel pairs, anticipated by CMD runs, is a realistic atomistic process occurring in TiN. Further studies are required in order to determine the kinetics of these events with higher reliability.

Frenkel-pair 0-K dissociation energies $E_{\text{diss}}^{\text{F}}$ are systematically ~ 0.2 eV lower than $E_{\text{form}}^{\text{F}}$ for both classical and *ab initio* results (see Table III). This difference indicates that the dissociated $\text{N}^{\text{I}} - \text{N}^{\text{V}}$ state [Fig. 9(h)] is slightly more favored energetically than the $\text{N}^{\text{I}}/\text{N}^{\text{V}}$ pair [Fig. 9(b)]. Thus, once dissociation has occurred, the N^{I} is slightly more likely to diffuse further away from the vacancy site rather than returning to an anion position neighboring N^{V} . However, dissociation events are rare; all MD runs show that Frenkel-pair annihilation [see Figs. 9(c)–9(f)] is much more frequent. This is consistent with the high (with respect to the energy of defect-free TiN) 0-K formation energy of dissociated Frenkel pairs (see Table III).

V. DISCUSSION

The CMD and AIMD activation energies E_a and E'_a , and attempt frequencies A and A' of N^{I} and N^{V} diffusion are summarized in Table IV. The corresponding diffusion coefficients $D(T)$ [obtained from Eq. (4)], are listed in Table V. At all temperatures, $D^{\text{I}}(T)$ diffusion coefficients are larger

TABLE IV. Summary of attempt frequencies A , activation energies E_a , and their convolved values A' and E'_a for N^{I} and N^{V} diffusion, as determined in the present paper's CMD and AIMD runs.

Process	CMD	AIMD
N^{I} migration		
A (10^{13} s^{-1})	$0.45 (\times 1.9^{\pm 1})$	$3.94 (\times 4.5^{\pm 1})$
E_a (eV)	1.17 ± 0.13	1.46 ± 0.37
A' ($\text{cm}^2 \text{ s}^{-1}$)	$7.28 (\times 1.8^{\pm 1}) \times 10^{-4}$	$6.35 (\times 2.7^{\pm 1}) \times 10^{-3}$
E'_a (eV)	1.17 ± 0.13	1.47 ± 0.23
N^{V} migration		
A (10^{13} s^{-1})	$267 (\times 2.6^{\pm 1})$	–
E_a (eV)	3.65 ± 0.23	–
A' ($\text{cm}^2 \text{ s}^{-1}$)	$3.89 (\times 2.5^{\pm 1}) \times 10^{-1}$	$[D^{\text{V}}(3000 \text{ K})] =$
E'_a (eV)	3.65 ± 0.23	$= 4.70 (\times 3.0^{\pm 1}) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$

TABLE V. Nitrogen self-interstitial and vacancy diffusion coefficient dependence on temperature as estimated via CMD and AIMD simulations. The AIMD D^V value is obtained from Eq. (3).

T (K)	D^I (cm ² s ⁻¹)		D^V (cm ² s ⁻¹)	
	CMD	AIMD	CMD	AIMD
1200	$8.9(\times 3.1^{\pm 1}) \times 10^{-9}$	—	—	—
1300	$2.1(\times 2.9^{\pm 1}) \times 10^{-8}$	—	—	—
1400	$4.5(\times 2.7^{\pm 1}) \times 10^{-8}$	—	—	—
1500	$8.5(\times 2.6^{\pm 1}) \times 10^{-8}$	—	—	—
1600	$1.5(\times 2.5^{\pm 1}) \times 10^{-7}$	—	—	—
1700	$2.5(\times 2.4^{\pm 1}) \times 10^{-7}$	—	—	—
1800	$3.9(\times 2.3^{\pm 1}) \times 10^{-7}$	—	$2.3(\times 5.0^{\pm 1}) \times 10^{-11}$	—
1900	$5.7(\times 2.2^{\pm 1}) \times 10^{-7}$	—	$8.1(\times 4.8^{\pm 1}) \times 10^{-11}$	—
2000	$0.8(\times 2.2^{\pm 1}) \times 10^{-6}$	$1.2(\times 4.9^{\pm 1}) \times 10^{-6}$	$2.5(\times 4.5^{\pm 1}) \times 10^{-10}$	—
2100	$1.1(\times 2.1^{\pm 1}) \times 10^{-6}$	$1.9(\times 4.7^{\pm 1}) \times 10^{-6}$	$6.8(\times 4.3^{\pm 1}) \times 10^{-10}$	—
2200	$1.5(\times 2.1^{\pm 1}) \times 10^{-6}$	$2.7(\times 4.5^{\pm 1}) \times 10^{-6}$	$1.7(\times 4.2^{\pm 1}) \times 10^{-9}$	—
2300	$2.0(\times 2.0^{\pm 1}) \times 10^{-6}$	$3.8(\times 4.3^{\pm 1}) \times 10^{-6}$	$3.9(\times 4.0^{\pm 1}) \times 10^{-9}$	—
2400	$2.5(\times 2.0^{\pm 1}) \times 10^{-6}$	$5.2(\times 4.2^{\pm 1}) \times 10^{-6}$	$8.4(\times 3.9^{\pm 1}) \times 10^{-9}$	—
2500	$3.2(\times 2.0^{\pm 1}) \times 10^{-6}$	$6.9(\times 4.1^{\pm 1}) \times 10^{-6}$	$1.7(\times 3.8^{\pm 1}) \times 10^{-8}$	—
2600	$3.9(\times 1.9^{\pm 1}) \times 10^{-6}$	$9.0(\times 3.9^{\pm 1}) \times 10^{-6}$	$3.3(\times 3.7^{\pm 1}) \times 10^{-8}$	—
2700	$4.8(\times 1.9^{\pm 1}) \times 10^{-6}$	$5.2(\times 3.8^{\pm 1}) \times 10^{-6}$	$6.0(\times 3.6^{\pm 1}) \times 10^{-8}$	—
2800	$0.6(\times 1.9^{\pm 1}) \times 10^{-5}$	$1.2(\times 3.7^{\pm 1}) \times 10^{-5}$	$1.0(\times 3.5^{\pm 1}) \times 10^{-7}$	—
2900	$0.7(\times 1.8^{\pm 1}) \times 10^{-5}$	$1.4(\times 3.7^{\pm 1}) \times 10^{-5}$	$1.8(\times 3.4^{\pm 1}) \times 10^{-7}$	—
3000	$0.8(\times 1.8^{\pm 1}) \times 10^{-5}$	$1.7(\times 3.6^{\pm 1}) \times 10^{-5}$	$2.9(\times 3.3^{\pm 1}) \times 10^{-7}$	$4.7(\times 3.0^{\pm 1}) \times 10^{-7}$

than $D^V(T)$ by a few orders of magnitude. However, N^I point-defects are in minority compared to N^V due to much larger formation energies [69]. In order to assess the effective contribution of N^I and N^V point-defects to mass transport in bulk TiN, it is necessary to estimate their concentration resulting from typical synthesis conditions, and weight it by the corresponding diffusion coefficient. Since the present paper's MD diffusion activation energies are in good agreement with the 0-K DFT estimations [19], it is reasonable to assume that $D^I(T)$ and $D^V(T)$ follow an Arrhenius trend over the temperature range 0–3000 K. Accordingly, 300-K diffusion coefficients can be obtained from the activation energies and prefactors listed in Table IV.

At a temperature T and pressure P , the equilibrium concentration c^X of a point defect X can be expressed as [93]

$$c^X(P, T) = g^X \exp[-G_{\text{form}}^X(P, T)/(k_B T)], \quad (6)$$

for which $G_{\text{form}}^X(P, T)$ is the defect free energy of formation and g^X is the number of degrees of internal freedom of X located at a lattice site ($g^X = 1$ for a monovacancy and $g^X = 6$ for $\langle 110 \rangle$ -oriented N^I/N^{lattice} dimers). The evaluation of formation free energies requires the calculation of vibrational and electronic entropy degrees of freedom. This is beyond the scope of this paper. However, a reasonably good estimation (at least serving the purpose of determining the relative contribution of N^I and N^V defects to mass transport as a function of temperature) of $c^I(P, T)$ and $c^V(P, T)$ curves can be provided by substituting $G_{\text{form}}^X(P, T)$ with $E_{\text{form}}^X(P, T)$ and accounting for the nitrogen chemical potential μ_N dependence on temperature and pressure.

Chemical potentials μ correspond to the energy of the reservoir with which the bulk system exchanges

atoms, thus forming or annihilating point-defects. For gases like N_2 , μ_N varies widely with temperature and pressure: [93]

$$2\mu_N(P, T) = E(N_2) + k_B T \left[\ln \left(\frac{P V_Q}{k_B T} \right) + \ln \left(\frac{\sigma B_0}{k_B T} \right) \right] + \mu_{\text{vib}}, \quad (7)$$

for which $V_Q = [h^2/(2\pi m_{N_2} k_B T)]^{3/2}$ is the quantum volume, σ is a symmetry factor ($=2$ for the N_2 molecule), and $B_0 = h^2/(4\pi^2 m_N d(N, N))$ is the rotational constant. The vibrational contribution μ_{vib} to the chemical potential $\mu_N(P, T)$ shall not be considered here, since it is also neglected for the bulk phase [93].

The sputtering depositions of Ref. [68] constitute suitable examples of layer-by-layer growth of single-crystal stoichiometric TiN thin films in N_2 atmosphere occurring in conditions relatively close to equilibrium. These experiments employ deposition temperatures of approximately 1000 K (within the optimum range for epitaxial growth of single-crystal TiN(001) layers [94]), low growth rates (~ 1 nm/min), and low energy of impinging particles. N_2 partial pressures P_{N_2} are of the order of $\sim 10^{-2}$ – 10^{-1} Pa.

While the pressure P does not affect the bulk free energy significantly, this should be chosen appropriately for a N_2 gas reservoir. Fixing $P_{N_2} = 10^{-1}$ Pa [68], the $\Delta\mu_N$ dependence on T is close to linear. From Eq. (7), one obtains $\Delta\mu_N = \mu_N(1000 \text{ K}) - \mu_N(0 \text{ K}) \simeq -1.5 \text{ eV}$. The variation of μ_N with temperature is expected to affect the magnitude of $G_{\text{form}}^X(P, T)$ values more than that induced by (here neglected) vibrational and electronic entropy terms of defective and defect-free bulk TiN. The temperature-dependent energy of formation of N^I and N^V point-defects can be obtained from

FIG. 11. (Color online) Estimated N^I and N^V effective contribution to mass transport in bulk TiN between 300 and 1500 K. Upper/lower curves of the same type define upper/lower uncertainty limits.

the expression: $E_{\text{form}}^X(P = 0.1 \text{ Pa}, T) = E_{\text{TiN}+X}(T = 0 \text{ K}) - E_{\text{TiN}}(T = 0 \text{ K}) + \varepsilon \cdot \mu_N(P = 0.1 \text{ Pa}, T) \simeq E_{\text{TiN}+X} - E_{\text{TiN}} + \varepsilon \cdot [\mu_N^{T=0\text{K}} - \frac{3}{2}10^{-3}\text{eV} \cdot (T/\text{K})]$, for which $\varepsilon = +1$ for N^V , -1 for N^I . In the temperature window 0–1000 K, the N^I formation energy increases, while that of N^V decreases by approximately 1.5 eV. Using the 0-K DFT E_{form}^V and E_{form}^I estimations of Tsetseris *et al.* [69], we arrive at the relationships:

$$c^I(T) = 6 \cdot \exp \left\{ -[4.6 + (\frac{3}{2}10^{-3} \cdot T/\text{K})]\text{eV}/(k_B T) \right\}, \quad (8)$$

$$c^V(T) = \exp \left\{ -[2.4 - (\frac{3}{2}10^{-3} \cdot T/\text{K})]\text{eV}/(k_B T) \right\}. \quad (9)$$

The N point-defect concentrations calculated from Eqs. (8) and (9), for a deposition temperature of 1000 K, and for a N_2 atmosphere with partial pressure $P = 0.1 \text{ Pa}$, are $c^I \simeq 10^{-30}$ and $c^V \simeq 3 \times 10^{-5}$, in qualitative agreement with the N^V concentration ($c^V < 5 \times 10^{-3}$) estimated for the as-deposited TiN thin films from electrical resistivity measurements [68]. By multiplying these concentrations with D^V and D^I diffusion coefficients [$c^X(1000 \text{ K}) D^X(T)$], we find that the effective contribution to mass transport of N^V is much larger than that of N^I at all temperatures (see Fig. 11). The difference increases monotonically with temperature. We note that $c^I(T)$ and $c^V(T)$ values, as estimated from Eqs. (8) and (9), become progressively less reliable as the temperature rises. This is due to increasingly large contributions of the $T \cdot S_{\text{form}}^X$ term [neglected in Eqs. (8) and (9)] to $G_{\text{form}}^X(P, T)$. Nevertheless, the inclusion of entropy in the evaluation of $c^I(1000 \text{ K})$ and $c^V(1000 \text{ K})$ is not expected to change qualitatively the trends of the curves in Fig. 11.

Beside the fact that lattice defects are generated during synthesis, the thermodynamics principles predict that a certain concentration of point-defects is present at thermal equilibrium. However, thermodynamics does not state which physical processes lead to point-defect generation. The spontaneous formation of Frenkel pairs, followed by Frenkel-pair dissociation, observed in the present paper's MD simulations, is one of the possible pathways for N^I and N^V creation in stoichiometric TiN. This does not imply that the equilibrium

FIG. 12. (Color online) Calculated (the present paper's CMD and AIMD D values) and experimental nitrogen diffusion coefficients in bulk B1 TiN. MD D^I and D^V results correspond to N self-interstitial and N vacancy diffusion coefficients. Experiments 1 and 2 curves are from Ref. [16]. Experiments 3 and 4 D results are from Ref. [18]. Experiments 5–8 diffusion coefficients are from Ref. [17].

concentration of N self-interstitials (c^I) and that of N vacancies (c^V) are equal, as N^I may quickly reach the surface (or grain boundaries in polycrystalline TiN), thus lowering the free energy of the system. While the AIMD results confirm the validity of the CMD predictions for N^I and N^V diffusivities, MEAM and DFT Frenkel-pair 0-K formation energies, as well as AIMD and CMD Frenkel-pair formation rates at $T > T_{\text{melt}}$ are significantly different, thus suggesting that CMD Frenkel-pair formation rates at $T < T_{\text{melt}}$ are overestimated. Due to this, it is not possible to predict reliable $c^I(T)$ and $c^V(T)$ concentrations at the thermal equilibrium or provide estimates of the relative contribution to mass transport deriving from the exchange of neighboring N lattice atoms. The mass transport fluxes produced by $N-N^{\text{Exc}}$ events (following the spontaneous formation of Frenkel pairs), as well as by migration of N^I and N^V point-defects deriving from Frenkel-pair dissociation, are indicative of the inherent thermal stability of stoichiometric B1 TiN.

Finally, it is useful to compare our D results for nitrogen self-diffusion in TiN with experimental findings available in the literature. It should be noted that the value of D determined experimentally depends directly on the concentration of point defects, which in our simulations is fixed to $\sim 1\%$. In addition, structural (internal stresses, extended defects, etc.) and chemical (point-defect relative concentration and spatial distribution, impurities, etc.) parameters affect point-defect mobilities in real systems. As a consequence the experimental D results range over several orders of magnitude.

Figure 12 is a plot of calculated and measured [16–18] point-defect diffusion coefficients for bulk TiN in various temperature ranges. Lines of same type and color define upper and lower D uncertainty range boundaries. At all temperatures, calculated N self-interstitial diffusion coefficients are larger than any measured $D(T)$ values by a few orders of magnitude.

This indicates that the experimental D values reported in references [16–18] should not be due to N^I diffusion.

Overall, calculated N^V diffusion coefficients are consistent with N point-defect mobilities determined experimentally. Our CMD $D^V(T)$ results are in good agreement with one of the $D(T)$ vs $1/T$ curves reported in Ref. [16] (compare light blue (CMD D^V) and purple (experiment 1) solid lines in Fig. 12). This is the same experiment that returned the E_a^V value (3.9 eV) in very good agreement with the present work estimation ($E_a^V = 3.65 \pm 0.23$ eV; see Sec. IV B). Calculated $D^V(T)$ values match quite closely also with those of experiments conducted by Anglezio-Abautret *et al.* [17] [compare light blue (CMD D^V) and black (experiment 7) solid lines in Fig. 12]. The latter agreement, however, is likely to be accidental. In Ref. [17], it is speculated that the measured diffusion coefficient values (black solid line in Fig. 12) are due to nitrogen self-diffusion along grain boundaries (not within grains as our results suggest) of polycrystalline $TiN_{0.94}$. Experimental $D(T)$ interpreted as due to nitrogen diffusion within TiN grains [17] are considerably smaller (see experiment 5 and experiment 6 lines in Fig. 12).

VI. CONCLUSIONS

Ab initio molecular dynamics based on DFT and CMD simulations provide atomic-level understanding of elementary diffusion processes in bulk $B1$ TiN, specifically for the migration of N vacancy and N self-interstitial point-defects in the dilute limit. Our determined set of TiN MEAM-potential parameters, used in CMD simulations, returns point-defect jump rates in good agreement with AIMD predictions, while yielding an excellent description of bulk TiN_x ($\sim 0.7 < x \leq 1$) structural, elastic, and thermal properties. The reliability of the classical model potential is shown and used in CMD simulations to obtain nitrogen point-defect activation energies E_a and attempt frequencies A , as well as diffusion coefficients D as a function of temperature. The N self-interstitial stable position in TiN is in dumbbell split-bond configurations formed with nitrogen lattice atoms. As studied with MD, after several random rotations about the N^I/N^{lattice} center of mass, which remains in the proximity of an anion lattice site, the N^I/N^{lattice} bond breaks, and one of the two N atoms migrates to a neighboring anion site by passing through metastable eightfold-coordinated tetrahedral positions. This process yields diffusion coefficients $D^I(T)$ with exponential prefactor $A' = 7.28 (\times 1.8^{\pm 1}) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and activation energy $E_a' = (1.17 \pm 0.13) \text{ eV}$. N vacancies,

considerably less mobile than N self-interstitials, move along $\langle 110 \rangle$ directions between neighboring anion sites yielding diffusion coefficients $D^V(T)$ with exponential prefactor $A' = 3.89 (\times 2.5^{\pm 1}) \times 10^{-1} \text{ cm}^2 \text{ s}^{-1}$ and activation energy $E_a' = (3.65 \pm 0.23) \text{ eV}$. Despite their higher mobility, N^I contribute to mass transport in TiN considerably less than N^V at all temperatures, due to much lower N^I concentrations. Moreover, our CMD simulations performed at $T \geq 1500 \text{ K}$ reveal an unanticipated atomistic process for defect-free bulk $B1$ TiN, that is, the spontaneous formation of N-self-interstitial/N-vacancy pairs (Frenkel pairs). This occurs when a nitrogen lattice atom leaves its bulk site to bond to a neighboring nitrogen lattice atom. In most cases, N^I/N^V mutual annihilation occurs within a fraction of a nanosecond. About 50% of these processes result in the exchange of two nitrogen lattice atoms. Occasionally, one of the Frenkel-pair N^I/N^{lattice} atoms diffuses away from the vacancy site, thus producing permanent N^I and N^V point defects. The AIMD runs confirm the predictions of CMD for the occurrence of Frenkel-pair spontaneous formation, simple annihilation and annihilation resulting in $N-N^{\text{Exc}}$, and dissociation in stoichiometric TiN but indicate that CMD Frenkel-pair formation rates are largely overestimated.

ACKNOWLEDGMENTS

We are grateful to Dr. O. Hellman for useful discussions and suggestions. The calculations and simulations were performed with resources provided by the Swedish National Infrastructure for Computing (SNIC), on the Triolith, Matter, and Kappa Clusters located at the National Supercomputer Centre (NSC) in Linköping and on the Akka and Abisko clusters located at the High Performance Computing Center North (HPC2N) in Umeå, Sweden. P. Münger, K. Engström, S.-H. Ko, M. Lie, and P. Larsson at NSC are acknowledged for assistance with technical aspects. We gratefully acknowledge financial support from the Knut and Alice Wallenberg Foundation (Isotope Project No. 2011.0094), the Swedish Research Council (VR) Linköping Linnaeus Initiative LiLi-NFM (Grant No. 2008-6572), and the Swedish Government Strategic Research Area Grant in Materials Science on Advanced Functional Materials (Grant No. MatLiU 2009-00971 through Sweden's innovation agency VINNOVA). I.A.A. is grateful for the Grant from the Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005) and Tomsk State University Academic D. I. Mendeleev Fund Program.

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