ChinaRxiv

AI translation · View original & related papers at
chinarxiv.org/items/chinaxiv-202503.00150

Atomistic simulation study of the diffusion and growth mechanisms of Ti thin films on Si(100) surfaces for betavoltaic cell

Authors: Hanzi Zhang, Long Kaihong, Han Yunze, Shen Chuankai, Tu Menghe, Zhang Baoliang, Zhang Baoliang

Date: 2025-03-13T00:00:00+00:00

Abstract

The nucleation and growth behavior of Ti thin films on Si(100) surfaces at 500 K were investigated via molecular dynamics and Monte Carlo methods. The focus of this study was on the nucleation characteristics,growth mode, crystal structure and surface structure of the Ti thin films for use in betavoltaic cell. The results demonstrate that at the initial stage of deposition, mixing of Ti films with Si substrates occurs at the interface. The surface roughness of Ti films is influenced by the deposition atomic rate, which is associated with the crystal structure transition in the films, and the stable HCP grains in the films are frequently accompanied by an FCC laminated dislocation structure. As the deposition rate increased, the growth mechanism of the Ti films transitioned from a random orientation to a selective orientation. Furthermore, we recalculated the adsorption energies of Ti at different adsorption sites on the Si(100)p(2$×$2) surface. This was done to identify the optimal diffusion path of Ti atoms on the Si(100) surface, which was then found via the transition state search method.

Full Text

Preamble

Atomistic Simulation Study of the Diffusion and Growth Mechanisms of Ti Thin Films on Si(100) Surfaces for Betavoltaic Cells

Hanzi Zhang,[1] Kaihong Long,[1] Yunze Han,[1] Chuankai Shen,[1] Menghe Tu,[1] and Baoliang Zhang[1],* [1]China Institute of Atomic Energy, Beijing 102413, China

The nucleation and growth behavior of Ti thin films on Si(100) surfaces at 500 K were investigated via molecular dynamics and Monte Carlo methods, focusing on the nucleation characteristics, growth mode, crystal structure, and surface

morphology of the Ti thin films for application in betavoltaic cells. The results demonstrate that mixing of Ti films with Si substrates occurs at the interface during the initial deposition stage. The surface roughness of Ti films is influenced by the deposition atomic rate, which is associated with crystal structure transitions in the films, and stable HCP grains in the films are frequently accompanied by an FCC laminated dislocation structure. As the deposition rate increases, the growth mechanism of the Ti films transitions from random orientation to selective orientation. Furthermore, we recalculated the adsorption energies of Ti at different adsorption sites on the Si(100)p(2$×$2) surface to identify the optimal diffusion path of Ti atoms on the Si(100) surface, which was then determined via the transition state search method.

Keywords: deposition; Si(100); Ti; first-principles calculation; molecular dynamics

Introduction

The interface between silicon and transition metals has long been critically important in various engineering applications, including microelectronic systems [**?**] and nanotechnology [**?**]. The electrical, thermal, and mechanical response of the silicon/transition metal interface is paramount for the overall performance of engineered systems [**?**, **?**]. In recent years, the field of nuclear energy has experienced a surge of interest in betavoltaic cells [**?**, **?**, **?**]. Betavoltaic cells offer numerous advantages, including long operational lifetime, stable output, ease of integration, high energy density, and strong environmental adaptability. Consequently, betavoltaic cells represent an ideal alternative in situations where fossil fuels or chemical batteries are impractical, such as remote sensing in extreme environments, medical implantable devices, and microelectromechanical systems (MEMS) [**?**]. Tritium betavoltaics hold particular promise due to the high specific activity of solid tritium compounds, low shielding requirements, and relatively high availability as a byproduct of CANDU® nuclear reactors [**?**]. Numerous studies have investigated the incorporation of tritides into monocrystalline silicon transducers [**?**, **?**, **?**]. Tritiated titanium is renowned for its low decay ray energy, excellent chemical stability, and high safety. Titanium can adsorb and store tritium in solid-state form at pressures of approximately 1.33$×10^{-5}$ Pa, forming tritiated titanium. This phenomenon results in high storage density and rapid tritium absorption, with equilibrium ionization decompression occurring at approximately 10^{-5} Pa at room temperature [**?**]. Samples containing silicon/transition metal interfaces are prepared via various vapor-phase film growth techniques, and deposition of transition metals on monocrystalline silicon substrates typically results in polycrystalline film formation.

For tritium betavoltaic cells with three-dimensional micro- and nanostructured semiconductors, existing studies have loaded tritium directly onto semiconductors in gaseous form, which necessitates exploring the possibility of obtaining tritium-absorbing metal thin films with maximal surface area and uniform distribution within three-dimensional micro- and nanostructures to serve as tritium

carriers, thereby achieving higher radioisotope tritium content. Ti thin films, as the tritium-absorbing material in betavoltaic cells, directly influence the amount of tritium adsorbed and its diffusion path, thus affecting the energy conversion efficiency and output power density of the cell. The performance of tritium cells can be significantly improved by optimizing the Ti film preparation process.

Magnetron sputtering is a widely utilized technique for titanium film deposition. The preparation process substantially influences the surface morphology, grain size, and texture of Ti films, thereby significantly impacting their functional properties [**?**, **?**, **?**]. Sputtering power is an important factor that influences the microstructure of titanium films by controlling the atomic deposition rate. Chen et al. [**?**] demonstrated that the deposition rate significantly affects the microstructure of Ti films prepared by magnetron sputtering on Si(100) surfaces, with a transition from random orientation to (002) preferred orientation as the deposition rate increases. Researchers have observed nanoamorphous structures in titanium films, characterized by nanocrystals within an amorphous matrix. Chawla et al. [**?**] reported that titanium film grain size increased with increasing power and substrate temperature, observing preferred (101) and (002) orientations on glass substrates at 100 W and 150 W, respectively. In a related study, Han et al. [**?**] investigated the impact of sputtering powers ranging from 80 to 120 W on titanium thin films deposited in deep holes, finding that thin films tended to form columnar structures as sputtering power increased. P. Moskovkin et al. [**?**] reported that at the lowest power density, the c-axis of α-Ti[001] is perpendicular to the substrate with the (002) plane parallel to the substrate. As discharge power density increases during deposition, additional Ti planes (100) parallel to the substrate appear, and at the highest power density, a (100) plane parallel to the substrate is predominantly observed. These structural changes affect film hardness; however, the cause of the (100) plane peak remains unclear. While these studies have proposed hypotheses regarding the nucleation and growth mechanism of Ti films on Si(100) substrates, further research is needed to investigate this deposition process.

Atomic-scale simulations, including density functional theory (DFT), molecular dynamics (MD), and Monte Carlo (MC) simulations, have proven valuable for investigating atomic-scale behavior at metal/ceramic interfaces, as well as for obtaining interfacial energetics [**?**, **?**, **?**], heat transport properties [**?**], and dynamic processes at surfaces and interfaces [**?**, **?**]. The first-principles method is highly accurate for determining energy changes and electronic information in small system models. The team led by Rafael Añez employs first-principles calculations to investigate Ti atom adsorption on Si(111) and Si(100) surfaces [**?**, **?**, **?**], analyzing interatomic interactions at the TiSi interface from a thermodynamic perspective. Their results indicate that TiSi interface mixing is enhanced by defect regions on the substrate surface, emphasizing the importance of Si diffusion in determining the structure of the TiSi mixed layer.

Over the past decade, MD simulations for plasma-surface interactions have emerged as crucial tools for investigating plasma phenomena including sputter-

ing, etching, injection, and deposition [**?**, **?**, **?**, **?**]. These simulations can replicate nucleation and growth behaviors of thin films. While periodic boundaries are commonly employed in MD simulations, ensuring the model is sufficiently large to maintain simulation authenticity is highly important. Moreover, variations in element type and target structure within the simulation system can result in differences in interatomic potential functions [**?**]. Conventional MD simulations are typically limited to hundreds of nanoseconds due to constraints imposed by system size and interatomic potential functions, limiting the range of observable outcomes and making it challenging to capture slow but critical structural evolution processes. Monte Carlo (MC) simulations determine atomic displacement probabilities based on thermodynamic barriers, enabling broader phase space sampling and often facilitating faster attainment of thermal equilibrium for surface structures [**?**, **?**, **?**]. Among these algorithms, the primary advantage of the timestamped force-bias Monte Carlo (tfMC) method is its capacity to preserve temporal scale. Although tfMC does not explicitly incorporate time, it establishes a correlation between simulations and time scales by integrating deterministic forces acting on atoms into a stochastic algorithm for atomic displacement, resulting in a markedly increased acceptance rate of atomic displacement and thus accelerating equilibrium attainment in the simulated system. Reza Namakian and colleagues employed a sequential MD/time-stamped force-bias Monte Carlo (tfMC) algorithm to simulate copper (Cu) deposition on titanium nitride (TiN) substrates [**?**], observing and experimentally verifying the transformation of Cu films on TiN(001) substrates from body-centered cubic (BCC) to face-centered cubic (FCC) accompanied by nanotwin formation. They also identified distinct film growth mechanisms on TiN(111) surfaces at Ti-terminated and N-terminated ends. Gao et al. [**?**] reported significant variations in microstructures of Cu films deposited on different substrate surfaces, with more pronounced effects on the Si(100) plane and in the vertical arrangement of higher-position atoms on the (110) crystal plane, while specific deposition characteristics were observed on the (111) crystal face. Compared with the C(111) surface, top atoms exhibit a more pronounced annular distribution and relatively smooth surface. Considerable research has been conducted on MD simulations of Cu deposition on Si substrates [**?**, **?**]; however, studies on MD simulations for titanium films remain scarce.

This study aims to investigate the nucleation and growth mechanisms of Ti films on Si(100) substrates via computational simulation, focusing on analyzing the impact of different deposition energies on Ti film microstructure and the Ti nucleation and growth process on Si(100) substrates. Section 2 provides a comprehensive account of the computational methodology and model configuration. The principal simulation outcomes are presented and discussed in Section 3, followed by a summary in Section 4.

II. Computational Details

A. DFT Calculations

Density functional theory (DFT) calculations were performed using DS-PAW software [**?**]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional was employed to handle electron exchange-correlation. A plane-wave cutoff of 400 eV was utilized in all calculations, with a vacuum layer set to 15 Å in the Z direction of the geometry. The Methfessel-Paxton integration scheme was employed for sampling the Brillouin zone at Monkhorst-Pack special points [**?**]. Calculations were performed with an energy convergence criterion of 10^{-6} eV and a force convergence criterion of 0.01 eV $\cdot$ Å^{-1}. The atomic adsorption energy was determined through the following calculation:

$$E_{ads} = E_{Si(100)+nTi} - E_{Si(100)+(n-1)Ti} - E_{Ti}$$

where $E_{Si(100)+nTi}$ denotes the energy of the surface containing n adsorbed Ti atoms, $E_{Si(100)+(n-1)Ti}$ denotes the energy of the surface with (n-1) adsorbed Ti atoms, and E_{Ti} is the energy of the ground state of an isolated Ti atom.

To gain further insights into the adsorption and diffusion behavior of Ti on the Si(100) surface, this study employs the transition state search (TSS) method to calculate the optimal diffusion paths and corresponding energy barriers between different adsorption sites. The k-point mesh utilized for climbing-image nudged elastic band (CI-NEB) calculations was set at $6 \times 6 \times 1$, while the convergence criterion for energies was maintained at a constant value, and the criterion for forces was modified to 0.01 eV $\cdot$ Å^{-1}.

B. Model of Titanium Atom Deposition and Simulation Methodology

The MD simulations were conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [**?**]. A Si(100) surface structure was constructed as a substrate with the x, y, and z axes oriented in the [011], [011], and [100] directions, respectively, and with a model size of $69 \times 69 \times 154$ Å^3 containing a total of 12,960 Si atoms. The x- and y-directions were subject to periodic boundary conditions, enabling the substrate to be treated as an infinite flat plate in the xy-plane, while the z-direction was subject to a fixed boundary condition. The existence of dimers on the (100) surface of Si introduces a certain degree of randomness to the surface arrangement. To obtain the final substrate surface structure containing dimers for the atomic deposition simulation, initial surface relaxation of Si(100) was carried out under the NPT ensemble for 100 ps.

[Figure 1: see original paper] depicts the simulated surface model of Ti deposition on a single-crystal Si(100) substrate. The substrate is represented by a fixed layer, a temperature-controlled layer, and a free layer from bottom to top. The

fixed layer prevents momentum transfer when incident atoms collide with the substrate, thereby preventing model drift. The top eight layers of atoms in the substrate are designated as free layers, allowing unrestricted interactions with incident particles to simulate diffusion behavior at the Ti–Si interface during deposition. Upon impact with the substrate, incident particles interact with one another, imparting kinetic energy to the system. This energy is subsequently converted into latent heat of condensation, resulting in increased system temperature. To maintain constant temperature throughout the deposition process, different system combinations were employed for different model layers to regulate temperature within the system.

Relevant studies have demonstrated that the relaxation process in vapor deposition simulations significantly impacts the final microstructure of thin films. To more accurately simulate the growth behavior of Ti atoms on the Si(100) surface during deposition, this paper employs a simulation scheme combining the timestamped force-bias Monte Carlo (tfMC) method and MD. The tfMC approach does not consider atomic velocity; therefore, its practical significance lies in the sampling temperature of the system rather than traditional temperature. The key parameter for determining tfMC simulation success is the maximum displacement length Δ of the lightest element in the system. A larger Δ results in a longer effective timescale for simulation; however, Δ must also be sufficiently small to meet equilibrium requirements. In this work, the properties of perfect lattice titanium and semiconductor silicon were tested separately, with results indicating that conditions with $\Delta\mathrm{Ti} = 0.1$ and $\Delta\mathrm{Si} = 0.1$ ensure increased sampling phase space while maintaining minimal precision loss.

C. Simulation of Titanium Atom Deposition

The deposition process is divided into two stages: the first involves mutual diffusion between Ti and Si atoms, whereas the second involves self-diffusion of deposited Ti atoms. To accurately depict deposition behavior and investigate film growth mechanisms, we utilize the Tersoff potential function developed by Plummer et al. [**?**] to describe interactions between Ti and Si, in conjunction with the EAM potential function developed by Mendelev et al. [**?**] to characterize interactions between Ti atoms. Prior to commencement of the formal simulation, validation of a hybrid scheme incorporating both potential functions was conducted. We assumed that the incident particle approaches the surface at a velocity perpendicular to it, with a Ti atom randomly emitted to the substrate within the incident layer depending on specific deposition parameters.

The velocity of the incident atom is determined by the given incident energy E_{in}, which can be calculated as follows:

$$v = \sqrt{\frac{2E_{in}}{m}}$$

where v represents the velocity of the incident particle and m represents the

mass of the incident particle. The incident energy range in this paper is 0.01 eV to 20 eV, with several values selected for simulation. shows the incident energy of the Ti atom.

The substrate temperature was set to 500 K during the thin-film deposition process. This temperature was selected based on its capacity to provide optimal kinetic energy for promoting film growth during Ti deposition. Diffusion behavior of Ti atoms is more significant at this temperature, affecting the orientation, nucleation, and growth process of the film, ultimately resulting in higher film quality. Furthermore, a series of control experiments were conducted at 300 K and 0.1 eV to investigate phase transition phenomena during Ti film growth. The system achieved thermal equilibrium by undergoing a 20 ps relaxation period under the NVE ensemble before deposition initiation. For the Nose–Hoover thermostat and Nose–Hoover barostat, the time constants for temperature and pressure relaxation toward desired values were set to 100 and 1000 times the timestep, respectively. A specified number of Ti atoms were randomly inserted in the deposition area, with each newly deposited atom required to be at least one cutoff radius (6.9 Å) away from previously deposited atoms. Following deposition completion, an NVT ensemble relaxation was employed to regulate temperature fluctuations resulting from kinetic energy transfer during successive collision events of deposited Ti atoms. To ensure comprehensive execution of both diffusion processes in the deposition simulation, 50 cycles were carried out, with 300 atoms per deposition cycle. Therefore, each cycle consisted of MD deposition, MD thermal balance, tfMC relaxation, and MD thermal balance. Visualization of all simulation results was performed via OVITO software. The surface atomic structure was analyzed via the polyhedral template matching (PTM) method, with the RSMD cutoff set to dimers on this surface at 1.68 eV, and these dimer structures are highly similar. Furthermore, the x, y, and z directions of the model correspond to the [010], [001], and [100] directions of the Si crystal, respectively. The dangling bonds on the bottom surface are saturated by hydrogen atoms. The bottom four layers of atoms are fixed in subsequent calculations to simplify the model, an approach demonstrated to be feasible on numerous occasions. Additionally, the k-point mesh utilized for calculations is set at $6 \times 6 \times 1$.

[Figure 2: see original paper] shows the Si(100) surface model, which comprises a tetrameric unit; the higher Si atom is designated by an orange-red color, whereas the other is designated by an orange-yellow color for ease of visual observation. The dimer structure of the Si(100) surface results in four distinct adsorption sites for individual Ti atoms on the periodic substrate, labeled with letters in Fig. 2. The adsorption energies of individual Ti atoms at different sites on the Si(100) surface are presented in .

III. Results and Discussion

A. Ti Diffusion Behavior on the Si(100) Surface

The cubic Si bulk was initially optimized, with energy and force convergence achieved under a Monkhorst-Pack mesh of 4 × 4 × 4 K-points. The optimized lattice constant is 5.47 Å, which agrees with results reported by Rafael Añez et al. [**?**] and experimental data (5.43 Å) [**?**], with an error of no more than 1%. The structure-optimized Si(100) surface, containing four Si dimer structures, is depicted in [Figure 2: see original paper]. The Si atoms in the dimers are shown in distinct colors for ease of differentiation. The structure was obtained by cell expansion and modification of the cut surface based on Si(100)p(2$×$2). The Si(100) surface model used in this work has a total of 8 atomic layers. The formation energy of the dimer structures on this surface is 1.68 eV, and these dimer structures are highly similar.

shows Ti adsorption energies (eV) at different sites. The results indicate that Ti atoms most favorably adsorb at the H-site, with an adsorption energy of -5.65 eV. Ti atoms at the H-site bond with Si atoms in the four surrounding dimers. There are two types of Ti-Si bonds, with bond lengths of 2.40 Å and 2.42 Å, as shown in Figure 3: see original paper. The bond length between Si atoms in the dimer increases as a consequence of Ti-Si atomic interactions. Concurrently, the asymmetry of Si atoms in the two dimers bonded to them is reduced because of Ti atom adsorption at the HDB sites. Nevertheless, the atomic environments of the two are not equivalent, and the Ti–Si bond lengths remain different, measuring 2.67 Å and 2.53 Å. This is not consistent with results reported by Rafael Añez et al., a discrepancy attributable to the larger periodic unit of the surface model in this paper. The structures of Ti atoms adsorbed at the H and HDB sites exhibit relatively low symmetry, influenced by the presence of neighboring dimers. Consequently, the calculations presented in this paper are more consistent with the adsorption properties of individual Ti atoms on the Si(100) surface. When the Ti atom adsorbs on the BL site, the Si atoms bonded to the Ti atom exhibit three distinct atomic environments. The Ti atom interacts with Si atoms on the two subsurfaces of the nondimer ([Figure 3: see original paper]e, f) with a bond length of 2.60 Å. Furthermore, this Ti atom bonds to Si atoms of the two neighboring dimers, which have different atomic environments. In contrast to the surface model presented in Refs. [**?**], the adsorption sites are positioned as far as possible within the interior of the model rather than on periodic boundaries, ensuring acquisition of more realistic adsorption energy data.

Changes in Ti-Si bond length affect the electron density distribution and local geometry between them, which in turn changes the electron supply capacity of the adsorption sites. In cases of short Ti-Si bond lengths, increased electron density in the vicinity of Ti atoms further facilitates electron transfer from the adsorption sites, thus decreasing adsorption energy. Conversely, as Ti-Si bond length increases, electron density decreases and adsorption energy is relatively

elevated.

Precise calculation of individual Ti atom adsorption energies enabled determination of the minimum energy paths for diffusion of Ti atoms from the first nearest neighboring HDB and BL sites to the H site. Five points were set between initial and final positions via linear interpolation. The transition state search results are presented in [Figure 4: see original paper]. Diffusion of Ti atoms from the HDB site to the H site necessitates crossing the Si atoms in the two dimers to which they are bonded. As previously discussed, the two Si atoms regain some symmetry under the influence of the Ti atom at the HDB site. Consequently, at this juncture, Ti atoms diffuse in a roughly linear trajectory toward the H site. The system energy reaches its maximum when the Ti atom is directly above the two Si atoms. Notably, the calculated shortest diffusion path from the BL site to the H site reveals that Ti atoms must traverse two potential barriers throughout the entire process. The Ti atoms initially reach the first nearest-neighbor HDB site and subsequently diffuse to the most stable H site. These results indicate that Ti atom adsorption at the H site on the Si(100) surface is highly stable and that Ti atom diffusion requires overcoming a high potential barrier.

B. Molecular Dynamics/Monte Carlo Simulations of Ti Deposition

[Figure 5: see original paper] shows island growth patterns during the initial stages of film deposition at different incident energies: (a-c) 0.1 eV, 4–6 loop; (d-f) 5 eV, 4–6 loop. In accordance with the deposition scheme outlined in Section 2, we deposited 15,000 atoms on the Si(100) surface in approximately 25 layers, considering an incident atomic energy interval of 0.1 eV to 5 eV. The figure illustrates initial island growth and island aggregation behavior of Ti films at incident energies of 0.1 eV and 5 eV. To quantify changes in deposition structure over time, we used the number of simulated cycles as a proxy for simulation time. At the beginning of deposition simulation, Ti atoms readily form 3D islands locally (Figure 5: see original paper) because of Ti adsorption on the Si(100) surface. At low-energy incidence, islands gradually coalesce, resulting in two-dimensional growth in the xy plane with minimal change in island height. As islands continue to grow two-dimensionally, film thickness increases. The islands merge and gradually wet the entire substrate, as illustrated in Figure 5: see original paper and Figure 5: see original paper. In the case of high-energy incidence, the distribution of Ti atoms is slightly deeper, as shown in Figure 5: see original paper. In other words, the surface is covered with Ti atoms at an earlier stage in high-energy incidence, leading to subsequent film growth occurring at a faster rate. In the later stage, stacking of Ti atoms becomes the primary growth mode, resulting in a notable increase in film growth rate [**?**].

In addition, the layer coverage of Ti and Si atoms near the Ti–Si interface (position Z = 60) was quantified ([Figure 6: see original paper]). To eliminate the possibility of random results, coverage was compared between the 20% and 80% intervals. The results show that diffusion of Si and Ti is not significant

in the low-energy deposition state. When incident energy is high, Ti atoms produce a better ion implantation effect. As a d-element, the lower mixing ratio of Ti to Si is analogous to the Co to Si study [**?**]. Despite the lower mixing ratio at the interface, a minimal quantity of Si still exerts influence on Ti film growth. The detachment of Si forms irregular defects at the interface that may act as sites for preferential nucleation of Ti atoms. Following the initial nucleation event, deposition of Ti atoms continues around these defect sites, resulting in a film growth pattern that exhibits specific orientations or the formation of early grain boundaries and stress concentration regions.

[Figure 7: see original paper] shows the evolution of crystal structure in Ti films as a function of simulation time at different incident energies. The results demonstrate that Ti films deposited on Si(100) surfaces at 500 K eventually form the HCP structure, which accounts for up to 60% of the crystal structure statistics. At high sputtering power, Ti migrates on the substrate surface and occupies available equilibrium positions on the pre-existing titanium film lattice, resulting in columnar structure formation [**?**]. The film grows at an inclined angle, consistent with other studies [**?**]. During initial deposition stages, Ti films predominantly exhibit the BCC phase. After 10 cycles, the substrate surface becomes covered with Ti atoms, indicating that Ti thin film growth had entered the Ti stacking phase. At this stage, the formed Ti film is influenced by the surface structure of the Si(100) substrate. The atomic arrangement is looser, and space utilization is lower, with Ti films forming local BCC structures on the surface. These structures act as buffer regions between subsequent HCP structures and the Si substrate until HCP structures at higher locations reach a certain level before disappearing. Notably, the stable growth phase of HCP structures is often accompanied by formation of FCC layer defects, which greatly enhance HCP structure stability. At an incident atomic energy of 20 eV, higher deposition energy leads to more pronounced local emergence of the BCC structure. Owing to the more active local atomic environment, formation of FCC layer defects was not observed in the initial HCP structures. These structures remain unstable and undergo significant compositional fluctuations during further deposition and relaxation processes.

The surface topographies of Ti films at different incident energies were analyzed, showing that four surfaces at lower energies (Figure 8: see original paper) exhibited similar surface topographies and banded grains oriented in both the (002) and (101) directions. This is due to earlier formation of layer mismatches in films under low-energy deposition, which leads to incomplete relaxation of the crystal structure. The Ti film at an incident energy of 20 eV in Figure 8: see original paper has larger grains, and films deposited with 20 eV incident energy exhibited uniform (101) surface orientation, suggesting that the (101) surface has higher priority than the (002) surface at high temperatures (500 K). This finding is consistent with Chawla et al. [**?**].

To further illustrate the effect of incident energy on surface quality, this paper employs surface roughness as a metric to quantify this difference. Surface

roughness is a common descriptor of film microscopic morphology that affects film properties. Typically, lower surface roughness corresponds to greater resistance and oxidation resistance. As incident energy increases, surface roughness also increases, altering diffusion paths and nucleation mechanisms of Ti atoms to some extent. The presence of diverse nucleation sites on high-roughness surfaces results in more randomized and denser Ti nucleation. Additionally, concave and convex structures on rough surfaces prolong atom retention time, potentially contributing to emergence of three-dimensional island growth modes and influencing overall film quality and homogeneity. In the molecular dynamics simulations presented in this paper, surface roughness was calculated from the z-coordinate of atoms on the film surface, expressed by the root-mean-square roughness R:

$$R = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - \bar{Z})^2}{N}}$$

where i represents the surface atom of the deposition layer and N is the total number of such atoms. Z_i represents the height of the surface atom of the deposition layer, whereas $\bar{Z}$ denotes the average height of all surface atoms. The resulting calculations are presented in [Figure 9: see original paper].

The results demonstrate that incident atomic energy profoundly influences the final surface roughness of Ti films. At lower energy states, increasing incident atom energy has a markedly beneficial effect on film surface roughness; however, this effect diminishes as incident energy increases from 0.1 eV to 5 eV, reaching a plateau. When incident energy was increased to 20 eV, surface roughness decreased further to 0.97. We believe the first decrease in surface roughness is primarily due to surface diffusion of Ti atoms during deposition, while the second decrease results from grain merger at high energy. Incident energy of deposited atoms exerts pronounced influence on film surface roughness. Increased surface roughness can facilitate formation of additional sites for tritium adsorption; however, larger surface roughness also generates more intricate nucleation sites during film growth, potentially influencing intrinsic film properties including thickness uniformity and grain size. We therefore contend that a distributed deposition method can be employed to regulate film quality by utilizing different incident energies throughout the deposition process.

C. Ti Diffusion Behavior on the Si(100) Surface

Selective surface orientation behavior generally occurs during Ti thin film deposition. Moskovkin et al. [**?**] revealed that during deposition, the Ti(002) plane parallel to the substrate is generated in low-energy states, whereas the (100) plane parallel to the substrate is mainly observed in high-energy states. To investigate the reasons for this phenomenon, we conducted deposition simulations at 300 K and 0.1 eV, obtaining surfaces containing (002) planes without (100) planes. The results are shown in Figure 10: see original paper. Unlike

the 500 K simulation, this simulation produced no BCC nanocrystals, indicating that the Ti (100) surface orientation is generated by BCC nanocrystalline phase transformation. This transformation process, shown in Figure 10: see original paper, is consistent with the mechanism of Ti metal phase transformation [**?**, **?**]. During the phase transition, the lattice undergoes large deformation along the β[110] direction. Since the film has larger relaxation space in the Z-axis direction, the $\beta \rightarrow \alpha$ phase transition tends to align the α(100) plane parallel to the substrate rather than the (002) plane, resulting in preferential formation of the (100) plane.

In addition, we calculated the surface energies of BCC(110), HCP(002), and HCP(100). The surface energies of HCP-Ti and BCC-Ti are given by:

$$\gamma = \frac{E_{slab} - N_{slab} \cdot E_{bulk}}{2A}$$

where A is the surface area, E_{slab} is the slab energy with N_{slab} atoms, and E_{bulk} is the bulk energy per atom. The factor of 2A accounts for the two surfaces of a slab.

In calculating surface energy, we adopted a cutoff energy consistent with that mentioned above and tested convergence with different layers and k-points. The final calculation results are shown in . These results indicate that α(100), as a close-packed surface of HCP-Ti, has higher surface energy. We believe that lattice deformation caused by phase transition is the direct cause of selective surface orientation, while energy stability of the surface is the fundamental cause. Ambient temperature during thin film deposition impacts the crystal structure and surface orientation of the resulting film. To enhance energy conversion efficiency and output power density of tritium cells, it is essential that metal films possess robust crystal structure and optimal surface orientation, enabling effective tritium adsorption and diffusion. It must be acknowledged that tritium adsorption and permeation-diffusion processes are highly complex, and further studies are required to ascertain the full extent of these effects. Our findings demonstrate, however, that experimenters can exert partial control over crystal structure and surface orientation of Ti metal films by regulating ambient temperature.

IV. Conclusion

The objective of this work is to investigate the diffusion and deposition behavior of Ti on the Si(100) surface at the atomic scale through atomic-scale simulations. A more realistic surface model was employed to calculate adsorption energies of Ti atoms at different adsorption sites on the Si(100) surface, resulting in identification of the optimal path for Ti atom diffusion on the surface. Atomic deposition simulation results indicate that Ti atoms strongly prefer to occupy the entire surface, with this process regulated by two-dimensional diffusion of Ti atoms. Nucleation of Ti films is influenced by upward-diffusing Si atoms,

with stable HCP grains in the films often accompanied by an FCC laminated dislocation structure. The surface roughness of Ti films gradually decreases with increasing incident energy, which is related to crystal structure transitions in the films. Our study concludes that regulating incident energy during deposition can effectively control Ti film surface roughness, thereby influencing film thickness uniformity and grain size. In addition, the direct reason for (100) surface formation in the film is lattice deformation during BCC nanocrystalline material phase transition, and the fundamental reason is that the (100) surface itself has a more stable structure. By regulating ambient temperature during deposition, it is possible to influence crystal structure and surface orientation of Ti thin films, which is crucial for enhancing the performance of tritium betavoltaic cells.

V. Credit Authorship Contribution Statement

Hanzi Zhang: Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Visualization, Writing –original draft. Kaihong Long: Software, Validation, Formal analysis, Visualization, Writing –review & editing. Yunze Han: Conceptualization, Visualization. Chuankai Shen: Conceptualization, Visualization. Menghe Tu: Conceptualization, Validation, Investigation, Data curation, Writing –review & editing. Baoliang Zhang: Writing –review & editing, Supervision, Project administration, Funding acquisition.

VI. Acknowledgements

Supported by the Fund of the Department of Reactor Engineering Technology, CIAE (No. 248201). We are grateful to HZWTECH for providing computing resources.

References

[1] H.K. Cheemalamarri, S. Bonam, S.R.K. Vanjari et al., Ti/Si interface enabling complementary metal oxide semiconductor compatible, high reliable bonding for inter-die micro-fluidic cooling for future advanced 3D integrated circuit integration. J. Micromech. Microeng. 30, 105005 (2020). doi:10.1088/1361-6439/ab9f00

[2] N. Benito, C. Palacio, Growth of Ti-O-Si mixed oxides by reactive ion-beam mixing of Ti/Si interfaces. J. Phys. D: Appl. Phys. 47, 015308 (2014). doi:10.1088/0022-3727/47/1/015308

[3] G. Saheli, T. Kuratomi, I.C. Chen et al., Use of Si KLL in XPS to distinguish Ti silicides from a Ti/Si mixture in thin films. Auger shifts and the Auger parameter. J. Electron Spectrosc. Relat. Phenom. 234, 57-63 (2019). doi:10.1016/j.elspec.2019.04.004

[4] Z.Y. Zhao, Y Liu, B Zhou et al., Wettability and reaction-bonded silicon carbide (RBSC) by joining of Ti–Si eutectic alloy. Ceram. Int. 50, 21184-21192

(2024). doi:10.1016/j.ceramint.2024.03.227

[5] X.Y. Wang, J.M. Feng, H.J. He et al., Modified graphene by 1 MeV electron irradiation in betavoltaic cell. Nucl. Instrum. Methods Phys. Res., Sect. B. 554, 165410 (2024). doi:10.1016/j.nimb.2024.165410

[6] B. Han, Z.S. Wang, D. Neena, et al., Influence of N2 flow rate on structure and properties of TiBCN films prepared by multi-cathodic arc ion plating and studied with ion beam scattering spectroscopy. Nucl. Sci. Tech. 28, 59 (2017). doi:10.1007/s41365-017-0212-0

[7] J.C. Zhang, Y.C. Han, L. Ren et al., Design and Preparation of SiC Radiation Voltaic Isotope Battery. At. Energy Sci. Technol. 55, 182 (2021). doi:10.7538/yzk.2020.youxian.0896

[8] C.L. Zhou, J.S. Zhang, X. Wang et al., Review—Betavoltaic Cell: The Past, Present, and Future 10, 027005 (2021). doi:10.1149/2162-8777/abe423

[9] B.L. Ellis, H. Fritzsche, J. Patel et al., Titanium tritide films as betavoltaic power sources. J. Electron Spectrosc. Relat. Phenom. 71, 660-665 (2017). doi:10.1080/15361055.2017.1290952

[10] Y.Q. Yang, Y.S. Lei, Z.K. Zhong et al., Long-Term Stability of Betavoltaic Battery Model and Prototype Based on Tritium/C-Silicon PN Junction Devices. J. Isot. 34, 10-15 (2021). doi:10.7538/tws.2021.34.01.0010

[11] X. Li, G.Q. Wang, Y.Q. Yang et al., Initial Research in Composite Electrodes with Energy Storage Applied for Betavoltaic Isotope Battery. At. Energy Sci. Technol. 52, 175-180 (2018). doi:10.7538/yzk.2018.52.01.0175

[12] X.Y. Wang, J.M. Feng, H.J. HE et al., Effect of Different Modification Methods on the Output Performance of Graphene Betavoltaic Isotope Batteries. J. Isot. 37, 319-326 (2024). doi:10.7538/tws.2024.youxian.035

[13] X.G. Long, G. Huang, S.M. Peng et al., Hydrogen isotope effects of Ti, Zr metals. Fusion Sci. Technol. 60, 1568-1571 (2023). doi:10.13182/FST11-A12733

[14] W.F. Zhang, S. Liu, L.B. Wang et al., Properties of Ti and Ti-alloy film deposited by direct current magnetron sputtering. At. Energy Sci. Technol. 42, 933–937 (2008). doi:10.7538/yzk.2008.42.10.0933

[15] Z.Y.Wang, N. Yao, X. Hu, Structural and Optical Property of Titanium Oxide Film Prepared by Energy Filtering Magnetron Sputtering Technique. Int. J. Appl. Ceram. Technol. 13, 164-169 (2016). doi:10.1111/ijac.12425

[16] X. Chi, C.H. Song, J.F. Bao et al., Research progress of titanium-based thin films prepared by magnetron sputtering. Therm. Spray Technol. 12, 17-21 (2020). doi:10.3969/j.issn.1674-7127.2020.02.003

[17] A. Y. Chen, Y. Bu, Y. T. Tang et al., Deposition-rate dependence of orientation growth and crystallization of Ti thin films prepared by magnetron

sputtering. Thin Solid Films. 574, 71–77 (2015). doi:10.1016/j.tsf.2014.10.053

[18] V. Chawla, R. Jayaganthan, A.K. Chawla et al., Microstructural characterizations of magnetron sputtered Ti films on glass substrate. J. Mater. Process. Technol. 209, 3444-3451 (2009). doi:10.1016/j.jmatprotec.2008.08.004

[19] Y.Z. Han, S.J. Li, X. Li et al., Study on Process Parameters of Magnetron Sputtering Titanium Coating in Deep Porous Structures. ACS Omega. 9, 14551-14557 (2024). doi:10.1021/acsomega.4c00540

[20] P. Moskovkin, C. Maszl, R. Schierholz et al., Link between plasma properties with morphological, structural and mechanical properties of thin Ti films deposited by high power impulse magnetron sputtering. ACS Omega. 418, 127235 (2021). doi:10.1016/j.surfcoat.2021.127235

[21] R. Añez, A. Sierraalta, M.A. San-Miguel et al., Role of the Si–Si bond stability in the first stages of Ti diffusion on a Si(1 1 1) 2 × 1 surface: A periodic DFT study. Appl. Surf. Sci. 273, 496-501 (2013). doi:10.1016/j.apsusc.2013.02.068

[22] R. Añez, A. Sierraalta, L. Díaz et al., Periodic DFT study of Ti deposition on defective Si(100) surfaces. Appl. Surf. Sci. 335, 160-166 (2015). doi:10.1016/j.apsusc.2015.02.046

[23] R. Añez, M.A. San-Miguel and J.F. Sanz, Periodic DFT study of Ti deposition on defective Si(100) surfaces. Surf. Sci. 606, 754-761 (2012). doi:10.1016/j.susc.2012.01.006

[24] A. Giri, J.L. Braun and P.E. Hopkins, Effect of crystalline/amorphous interfaces on thermal transport across confined thin films and superlattices. J. Appl. Phys. 119, (2016). doi:10.1063/1.4953683

[25] Y. Gao, Q. Xie, T.H. Gao et al., Investigation of interfacial matching between 3C-SiC substrate crystals and its surface layer deposited Cu elements using molecular dynamics simulations. Surf. Interfaces. 43, 103600 (2023). doi:10.1016/j.surfin.2023.103600

[26] R. Namakian, B.R. Novak, X.M. Zhang et al., A combined molecular dynamics/Monte Carlo simulation of Cu thin film growth on TiN substrates: Illustration of growth mechanisms and comparison with experiments. Appl. Surf. Sci. 570, 151013 (2021). doi:10.1016/j.apsusc.2021.151013

[27] L. Ji, L. Liu, Z.W. Xu et al., Molecular dynamics simulation on the effect of dislocation structures on the retention and distribution of helium ions implanted into silicon. Nanotechnol. Precis. Eng. 3, 81-87 (2020). doi:10.1016/j.npe.2020.03.003

[28] Y.Y. Liu, Z.H. Shi, T.B. Liang et al., The mechanism of room-temperature oxidation of a HF-etched Ti3C2Tx MXene determined via environmental transmission electron microscopy and molecular dynamics. InfoMat. 6, e12536 (2024). doi:10.1002/inf2.12536

[29] X.L. Li, X. Zhang, Y.H. Xu et al., Molecular dynamics study of surface binding energy and sputtering in W-V alloys. Fusion Eng. Des. 195, 113971 (2023). doi:10.1016/j.fusengdes.2023.113971

[30] Y. Tang, J.K. Liu, Z.H. Yu et al., Molecular dynamics study on the dependence of thermal conductivity on size and strain in GaN nanofilms. Chin. Phys. B. 32, 066502 (2023). doi:10.1088/1674-1056/acbf26

[31] T. Li, Molecular dynamics simulations of droplet coalescence and impact dynamics on the modified surfaces: A review. Comput. Mater. Sci. 230, 112547 (2023). doi:10.1016/j.commatsci.2023.112547

[32] E.C. Neyts, A. Bogaerts, Combining molecular dynamics with Monte Carlo simulations: implementations and applications. Theor. Chem Acc. 132, 277-288 (2013). doi:10.1007/s00214-012-1320-x

[33] K.M. Bal, E.C. Neyts, On the time scale associated with Monte Carlo simulations. J. Chem. Phys. 141, (2014). doi:10.1063/1.4902136

[34] A. Papadopoulou, E.D. Becker, M. Lupkowski et al., Molecular dynamics and Monte Carlo simulations in the grand canonical ensemble: Local versus global control. J. Chem. Phys. 98, 4897-4908 (1993). doi:10.1063/1.464945

[35] J. Zhang, C. Liu, Y.H. Shu et al., Growth and properties of Cu thin film deposited on Si(001) substrate: A molecular dynamics simulation study. Appl. Surf. Sci. 261, 690-696 (2012). doi:10.1016/j.apsusc.2012.08.082

[36] S.F. Hwang, Y.H. Li and Z.H. Hong, Molecular dynamic simulation for Cu cluster deposition on Si substrate. Comput. Mater. Sci. 56, 85-94 (2012). doi:10.1016/j.commatsci.2012.01.010

[37] P.E. Blöchl, Projector augmented-wave method. Phys. Rev. B. 50, 17953 (1994). doi:10.1103/PhysRevB.50.17953

[38] J.M. Hendrik, D.P. James, Special points for Brillouin-zone integrations. Phys. Rev. B. 13, 5188 (1976). doi:10.1103/PhysRevB.13.5188

[39] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. 117, 1-19 (1995). doi:10.1006/jcph.1995.1039

[40] P. Gabriel, J.T. Garritt, Bond-order potentials for the Ti3AlC2 and Ti3SiC2 MAX phases. Phys. Rev. B. 100, 214114 (2019). doi:10.1103/PhysRevB.100.214114

[41] M.I. Mendelev, T.L. Underwood and G.J. Ackland, Development of an interatomic potential for the simulation of defects, plasticity, and phase transformations in titanium. J. Chem. Phys. 145, 154102 (2016). doi:10.1063/1.4964654

[42] C.R. Hubbard, H.E. Swanson and F.A. Mauer, A Silicon Powder Diffraction Standard Reference Material. J. Appl. Cryst. 8, 45-48 (1975). doi:10.1107/S0021889875009508

[43] H.D. Wang, M.L. Dong, X. Cui et al., Mechanical properties of nano Ti films with different thickness. J. Mater. Eng. 43, 50–56 (2015).

doi:10.11868/j.issn.1001-4381.2015.11.009

[44] N.I. Plusnin, A.P. Milenin and D.P. Prihod' ko, Formation of the Co/Si(111)7x7 interface: AES- and EELS-study. Appl. Surf. Sci. 166, 125-159 (2000). doi:10.1016/s0169-4332(00)00393-

[45] Y.J. Tang, J. Tao, H.J. Tao et al., Effects of deposition parameters on structures of sputtered Ti films and TiO2 nanotube arrays prepared by anodic oxidation. Rare Metal. Mater. Eng. 37, 2186–2190 (2008). doi:10.3321/j.issn:1002-185X.2008.12.027

[46] R. Alvarez, A. Garcia-Valenzuela, V. Rico et al., Kinetic energy-induced growth regimes of nanocolumnar Ti thin films deposited by evaporation and magnetron sputtering. Nanotechnology. 30, 475603 (2019). doi:10.1088/1361-6528/ab3cb2

[47] Y.Y. Cheng, C.C. Lee, Simulation of molecular dynamics roughness on an Al thin film. Surf. Coat. Technol. 203, 918-921 (2008). doi:10.1016/j.surfcoat.2008.08.011

[48] P. Moskovkin, C. Maszl, R. Schierholz et al., Link between plasma properties with morphological, structural and mechanical properties of thin Ti films deposited by high power impulse magnetron sputtering. Surf. Coat. Technol. 418, 127235 (2021). doi:10.1016/j.surfcoat.2021.127235

[49] R. Shi, V. Dixit, H.L. Fraser et al., Variant selection of grain boundary α by special prior β grain boundaries in titanium alloys. Acta Mater. 75, 156-166 (2014). doi:10.1016/j.actamat.2014.05.003

[50] N. Stanford, P.S. Bate, Crystallographic variant selection in Ti–6Al–4V. Acta Mater. 52, 5215-5224 (2004). doi:10.1016/j.actamat.2004.07.034

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.