

YE WANG

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Supervisors: Professor Veronika Zadin
 Institute of Technology, University of Tartu

 Professor Alvo Aabloo
 Institute of Technology, University of Tartu

 Associate Professor Sergei Vlassov
 Institute of Physics, University of Tartu

 Associate Professor Andreas Kyritsakis
 Institute of Technology, University of Tartu

Internal Reviewer: Associate Professor Artur Tamm
 Institute of Physics, University of Tartu

Opponent: Associate Professor Roberto Luis Iglesias Pastrana
 Department of Physics, University of Oviedo, Spain

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ABSTRACT

High electric fields exert a significant influence on the behavior of metal surfaces, leading to changes in interatomic interactions in a complex manner. This can induce various types of electric field-induced surface modifications, including biased surface diffusion, which results in subsequent vacuum breakdown, and field-induced surface restructuring.

The fundamental mechanisms of vacuum breakdown initiations remain incomplete. One of the most plausible explanations is the field-induced growth of nano-protrusions on metal surfaces by biased diffusion. Previous theories suggest that atomic diffusion is biased towards stronger electric fields under an electric field gradient, and the field-surface dynamics can be described by the effective dipole moments and polarizability of surface adatoms, neglecting hyperpolarizability (higher-order) terms.

Additionally, the mechanism of field-induced surface restructuring remains unknown. For example, scanning field emission microscopy (SFEM) experiments observed a 10% change in field-emitted current when the carburized tungsten structure was exposed to electric fields. Notably, changes in field-emitted current corresponding to a single surface step (approximately 2Å) typically result in a measurement variation of around 1%, suggesting a potential surface restructuring. However, the lack of the exact atomic structure of the R(15×12) surface limits the exploration of potential field-induced atomic structure modifications.

This thesis provides insight into the development of atomic-level simulation models for electric field-induced surface diffusion and restructuring. Firstly, biased self-diffusion on Cu surfaces in the presence of an electric field gradient was observed. This process contributes to the continuous replenishment of particle-emitting nanotips, which may result in the consequent vacuum breakdown. To investigate these phenomena, molecular dynamics (MD) simulations were performed and coupled with finite elements method (FEM) to introduce electric fields. To validate the MD-FEM model, I estimated the effective dipole moment and polarizability from the diffusion bias in MD simulations and compared them to the corresponding values obtained from density functional theory (DFT) calculations. The polarization characteristics derived from the MD-FEM model provide only qualitative evaluations compared to the values from DFT calculations. This difference confirms that while the developed MD-FEM approach is in the right direction, further exploration of other advanced methods is crucial. Secondly, the formulae used in DFT calculations, which disregard hyperpolarizability terms, have only been tested for fields up to 3 GV/m due to computational limitations of the plane-wave DFT basis. Given the significant importance of these polarization formulae, a question arises: can these reduced formulae be trusted for a much wider range of electric fields? Cu nanoparticles were used as test structures. Although such high fields significantly alter their entire structures, their total energies were precisely described by the effective dipole moment and polarizability, without the inclusion of hyper-order polarizability terms. This

demonstrates that these polarization formulae are valid for electric fields that exceed the range relevant for intense field emission and vacuum breakdown. Thirdly, SEFM experiments observed a 10% change in field-emitted current, rather than the expected 1%, on the carburized tungsten structure under high electric fields. At the same time, a 0.4 eV work function difference was also measured, indicating a field-induced surface restructuring. However, the unknown atomic structure of the carburized tungsten surface ($R(15 \times 12)$ -C/W(110)) limits further exploitation to reveal the mechanism of surface restructuring. In this thesis, I propose a new atomic structure model for the $R(15 \times 12)$ surface and then employ DFT and machine learning-based MD calculations to show that the proposed model is consistent with the experimental scanning tunneling microscopy (STM) imaging of the surfaces.

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LIST OF PUBLICATIONS

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- II. Wang, Y.; Kyritsakis, A.; Zadin, V. Polarization characteristics and structural modifications of Cu nanoparticles under high electric fields. *Frontiers in Physics*, 12, DOI: 10.3389/fphy.2024.1328478.
- III. Wang, Y.; Moradpur-Tari, E.; Zadin, V.; Kyritsakis, A. Unraveling the atomic structure of the R(15×12) reconstruction of carburized W(110) based on ab initio calculations. *Applied Surface Science*, 643, DOI: 10.1016/j.apsusc.2023.158632.

Other publication

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Authors Contribution

- In **publication I**, the author was responsible for all DFT simulations, data analysis and wrote the DFT part of the paper.
- In **publication II**, the author simulated all Cu nanoparticle models with DFT, analyzed the results, and wrote the original draft of the paper.
- In **publication III**, the author proposed the atomic structure of R(15×12) reconstruction, conducted simulations and analysis, and wrote the original draft of the paper.

ABBREVIATIONS AND SYMBOLS

DFT	Density function theory
MD	Molecular dynamics
FEM	Finite element method
CLIC	The compact linear collider
KMC	Kinetic Monte Carlo
STM	Scanning tunneling microscopy
SFEM	Scanning field emission microscopy
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
LCAO	Linear combinations of atomic orbitals
VASP	The Vienna Ab Initio Simulation Package
PAW	Projector augmented-wave
NVE	Microcanonical ensemble
NVT	Canonical ensemble
NPT	Isothermal-isobaric ensemble
NPH	Isoenthalpic-isobaric ensemble
NP	Nanoparticle
F_l	Strength of the electric field at the initial lattice site of the atom,
μ	Dipole moment
α	Polarizability
ΔE_m	Migration energy barrier change
$\langle x \rangle_b$	Expected displacement
Γ	The unbiased jump rates
$O(F^2), O(F^3)$	Hyperpolarizability terms
$\rho(r)$	Electron density
$V_{eff}(r)$	Effective potential
$V_{XC}(r)$	Exchange-correlation potential
$\{G\}, \{a_{i,k,G}\}$	Reciprocal lattice vectors and plane wave coefficients

CHAPTER 1

INTRODUCTION

Metal surfaces are subjected to high electric fields, and apart from experiencing mechanical stress and potential electron or ion emission, the diffusion dynamics of surface atoms can also be affected [1–4], leading to field-induced surface modifications. These modifications have significant implications, such as vacuum breakdown and surface restructuring.

Vacuum breakdowns, also known as vacuum arcs, can result from field-induced growth of surface protrusions by biased diffusion in high electric field gradients. Such breakdowns are detrimental to a wide range of technologies, including particle accelerators [5–7], fusion reactors, vacuum switches, electron sources, etc. [8–11]. The compact linear collider (CLIC) [12] at CERN is a critical example of a powerful particle accelerator where vacuum arcs may have a significant impact.

When an applied electric field is increased beyond a certain limit, violent discharges in the form of vacuum arcs are observed on single metal tip cathodes. These discharges indicate the presence of an inherent surface response mechanism that initiates arcs. However, the physical mechanism leading from intense field emission to the initiation of vacuum arcs is almost impossible to realize experimentally [13], primarily because arcs typically occur in the range of 10–50 GV/m [9]. The electric field magnitudes applied in vacuum arcing experiments (hundreds of MV/m) are too low for direct field electron emission, indicating the existence of local field enhancement, necessary to reach the level of fields involved in field emission. One of the most common hypotheses to explain this is the appearance of surface asperities or protrusions, for which the local field at the apex can be expressed as $F = \beta F_{ext}$, where $\beta \approx h/r$ is the geometry aspect ratio (height over apex radius) of the metal surface asperity and F_{ext} is the applied field [15–17]. Therefore, after exerting an applied field F_{ext} , the enhanced field F can eventually cause the metal tip (emitter) to melt, deform, and subsequently evaporate in the form of neutral atoms and charged nano-clusters into the vacuum. That leads to a positive feedback loop of self-reinforcing growth and heating of the tip, eventually leading to the ignition of plasma and vacuum arc [2,18]. Yet, the mechanisms that lead to the appearance of high aspect ratio surface protrusions remain unclear.

The biased diffusion of adatom on metal surfaces under electric fields has been studied extensively both experimentally and theoretically [19–25], and it is considered a potential mechanism for the growth of surface protrusions. Tsong and Kellogg demonstrated experimentally that the adatom migration is biased along the field gradient towards stronger fields [19,26]. Tsong et. al. proposed a theoretical model suggesting that the migration energy barriers of a surface

adatom in a non-uniform field are dependent on its atomic polarization characteristics, i.e. its effective dipole moment and polarizability [22,23]. To date, various models have been developed to tackle this phenomenon.

Jansson et. al. [27] developed a general Kinetic Monte Carlo (KMC) model and observed the diffusion-driven growth of surface nanotips in the presence of high electric field gradients. They identified a mechanism where nanotips may start forming on metal surfaces due to biased atom diffusion, demonstrating good agreement with experiments. Although numerous challenges in applying KMC simulations to the Cu surface have been identified [28,29], a significant portion of these issues arise from the assumption of a rigid lattice with fixed lattice sites. For example, on the face-centered cubic $\{1\ 1\ 1\}$ surface, the off-lattice hexagonal close-packed (hcp) sites often exhibit stability comparable to that of a regular lattice site. To overcome the intrinsic limitations of rigid lattice approximation in KMC, molecular dynamics (MD) methods may offer a more accurate description of these processes due to the length and time scale limitations, as well as the necessity of incorporating the effects of electric fields in MD simulations, Veske et. al. [30] developed a method that couples MD with a finite elements method (FEM) field solver. The biased self-diffusion of Cu adatoms on Cu surfaces in the presence of an electric field gradient was observed to verify the validity of the developed MD-FEM approach. However, adatoms on the $\{1\ 1\ 0\}$ surfaces require higher activation energy to migrate, approximately 0.5 eV. To assess the effect of biased diffusion on the three most common surfaces, the accelerated MD method was used for the $\{1\ 0\ 0\}$ orientation. By estimating the effective dipole moment and polarizability from the diffusion bias in the MD-FEM model and comparing these values to those obtained from density functional theory (DFT) calculations, it was found that the polarization characteristics derived from the MD-FEM model provide only qualitative evaluations compared to the values from DFT calculations.

The theory proposed by Tsong et. al. has recently been further developed in a rigorous manner by Kyritsakis et. al. [31,32], who found that to calculate these polarization characteristics correctly, it is not sufficient to consider only the atomic charges, but rather incorporate the redistribution of the charge density in the entire surrounding system of the atom, i.e. its local atomic environment. Although this developed method has proven effective in describing the polarization characteristics and the biased diffusion dynamics for low fields up to a few GV/m, it remains unclear whether higher-order hyper-polarizability terms can be neglected for higher electric fields. Cu nanoparticles were used as test structures, and the results demonstrate that their total energies are precisely described by the effective dipole moment and polarizability without including hyper-order polarizability terms.

Despite various theoretical findings on biased diffusion, experimental evidence remains limited. However, a recent study by Bertolini et. al. [33], which observed field-induced surface restructuring on the R(15 $\times$ 12) carburized tungsten structure, may support the hypothesis. In this experiment, a change of approximately 10% in the field emitted current, along with an approximately 0.4 eV work function

difference, was observed when studying the R(15×12) surface using different methods. In contrast, previous experimental measurements of a monatomic surface step (approximately 2Å) showed only an approximately 1% change in the field emitted current [34,35]. The observed 10% change, being two orders of magnitude larger than the expected 1% change, strongly suggests potential field-induced surface restructuring. Otherwise, such a significant difference would be difficult to explain. This discovery may hold the potential to unlock new pathways for further exploiting the electric-field-induced surface phenomena and provide valuable insights into carburized W(110) surfaces in the assembly of nano-scale patterns by the application of high electric fields.

The R(15×12) and the R(15×3) are two particular types of surface reconstructions of carburized W(110), formed when carbon (C) diffuses to W{110} surfaces at high annealing temperatures. Both exhibit nm-scale specific periodicities in their atomic structure. These surface periodicities, reflected in corresponding periodicities in chemical properties of the carburized surfaces, have been widely used as templates for the growth and self-organization of metal nanostructures [36–40]. In particular, the R(15×3) serves as a well-suited template for supporting the self-assembly of Au nanowires, C₆₀, nano-strips of transition metals, and fullerene molecular nano-clusters [39]. The self-organization on R(15×12) is more complex, as half of its surface is considered carbon-poor, and the other half carbon-rich. Ag and Co are found to nucleate at carbon-poor regions [36], while Au is deposited along the carbon-rich regions of the unit cell [37]. Based on these findings, the carburized W{110} surfaces are considered highly promising templates for nano-patterned functionalities with various possible applications, including nano-biosensors, drug design, nano-electronics, etc. Although these carburized W{110} surface structures attract extensive attention from both theoretical and experimental studies [41–49], their exact atomic structures remain unclear. The lack of this knowledge significantly limits the understanding of their properties, including their response under high electric fields, thus hindering the exploration of novel functionalities, as well as the ability to experimentally confirm their possible field-induced surface modifications. Therefore, there is an increasing need to find their exact atomic structures, specifically explaining the mechanism of the surface restructuring in the presence of electric fields at the atomic level. Understanding the exact atomic structure of the R(15×12) is crucial for unveiling the underlying mechanism.

1.1 Research Objectives

The purpose of this work is to investigate the properties of metal surfaces under the influence of external electric fields. High electric fields can affect the inter-atomic interactions of metal surfaces in a complex manner, leading to surface modifications such as field-induced biased surface diffusion and surface restructuring.

Firstly, surface adatom tends to drift towards stronger electric fields by biased diffusion, as has been observed both experimentally and theoretically. To overcome the intrinsic limitations of rigid lattice approximation in KMC simulations, alternative methods are required. The MD-FEM model tends to be an effective approach for studying the drift of Cu adatoms under electric field gradients. To verify the validity of the MD-FEM model, I estimate the diffusion characteristics of adatoms on Cu surfaces under fields and compare them to the ones predicted via the atomic polarization characteristics formulae as obtained from DFT calculations.

Secondly, these formulae are used to describe the biased diffusion of an adatom in non-uniform fields, and neglect higher-order hyper-polarizability terms. The validity of this approximation has thus far been successfully tested for low fields up to a few GV/m. To assess whether those hyperpolarizability terms can be neglected, I investigated the behavior of Cu nanoparticles under high electric fields (up to 15 GV/m), which are relevant to field emission and vacuum breakdown. I find that the first two terms in the formula are sufficient to evaluate polarization characteristics.

Thirdly, high electric fields can induce surface restructuring. When the carburized tungsten R(15×12) surface is subjected to high electric fields, an approximately 10% change in the field-emitted current is observed, which is two orders of magnitude larger than the expected 1% change. Additionally, a 0.4 eV work function difference measured by different methods, such as I(U) curve fitting, suggests a possible electric field-induced restructuring in atomic structure. However, the absence of the exact atomic structure information for the R(15×12) surface limits the exploration into potential field-induced phenomena. I here propose a new atomic structure for the R(15×12) surface.

1.2 Structure of this Work

The results of this thesis are published in the following papers:

Publication I: To investigate the self-biased diffusion of Cu adatoms under non-uniform electric fields, two common approaches are used: MD-FEM methods and DFT calculations. DFT calculations are particularly valuable for precisely obtaining atomic polarization characteristics. To validate the MD-FEM electrostatic model, I estimated polarization characteristics by fitting the migration barrier formula proposed by Tsong and Kellogg and compared them to corresponding values obtained from DFT calculations. The results indicate that while the MD-FEM model can only provide qualitative evaluations of polarizability, there is still a need to develop methods that can quantitatively evaluate polarization characteristics.

Publication II: Given the significant importance of the polarization characteristics, the validity of the formula used to obtain the effective dipole moment and polarizability has been tested only for low fields up to 3 GV/m. This limi-

tation arises from the plane-wave DFT basis sets. In this work, I used Cu nanoparticles as test structures to verify the validity of neglecting hyper-polarizability terms for a much wider range of applied fields, utilizing localized DFT basis sets. I compared the total energy calculated by DFT calculations with the total energy obtained by fitting the polarization characteristics formula. The verification confirms that disregarding hyper-polarizability terms is a valid approximation for fields up to 15 GV/m.

Publication III: When the carburized tungsten structure $R(15 \times 12)$ is exposed to a high electric field, a 0.4 eV work function change is measured by different methods, indicating a potential electric field-induced surface restructuring. However, the lack of understanding of its exact atomic surface structure limits the explanation of the work function difference. In this work, I proposed a new atomic structure of the $R(15 \times 12)$ surface. The proposed structure successfully reproduced the most characteristic features of the experimental STM images very well, showing a high correlation between the experimental and simulated surface STM images.

CHAPTER 2

COMPUTATIONAL METHODS

2.1 Density Functional Theory

2.1.1 General Concept

Quantum mechanics is a fundamental theory that describes the laws of motion for atoms, molecules, and sub-atomic particles, exhibiting both particle and wave properties depending on the experimental conditions. Quantum mechanics contains several foundational postulates, one of them being the Schrödinger equation, which states the quantum state of microscopic particles can be completely described by the equation,

$$\hat{H}\Psi = E\Psi \quad (1)$$

Solving the Schrödinger equation allows for the determination of the state wave function of the system, with exact solutions easily achievable for single-electron systems. However, when dealing with many-body problems, the interactions among electrons introduce complexity. For example, in a system comprising M nuclei and N electrons, the wave function involves $3 \times (M + N)$ independent variables. The interparticle interactions prevent the separation of variables, making it challenging to obtain an exact solution for the Schrödinger equation in such cases.

The Schrödinger equation can be approximately solved by reasonable approximations, and one commonly used method is the Born-Oppenheimer approximation [50,51], it is assumed that the motion of the nucleus and electrons can be treated independently, based on the significant difference in mass between electron and nuclei, as well as the significantly higher speed of electron movement compared to nuclei. The total wave function of the molecule is expressed as the product of the nucleation wave function and the electron wave function, with the coordinates of the nucleus treated as approximately fixed. While solving the electron motion equation has significant implications, the Born-Oppenheimer approximation simplifies the Schrödinger equation to $3N$ variables, yet it does not address the challenges posed by the interaction of multiple electrons.

Density functional theory (DFT) stands out as an exceptionally successful approach for solving the Schrödinger equation. The fundamental concept behind DFT is that the wave function and all system properties are uniquely determined by the electron density of the ground state. Within the DFT framework, a complex N -electron system can be characterized using 3-spatial-variable functions, thereby mitigating the computational challenge associated with $3N$ variables.

Modern Density Functional Theory (DFT) can be traced back to the two theorems proven by Hohenberg and Kohn. In this context, a concise introduction

was provided to the fundamental models and principles. The Thomas-Fermi model can be regarded as the prototype of DFT, and despite its inherent roughness, it has exerted significant influence on the development of the theory.

2.1.2 Thomas-Fermi (TF) Model

In 1927, Thomas [52] and Fermi [53] proposed the Thomas-Fermi model, with free electrons as the focus of their research. The model assumes that electrons are not subjected to external forces and do not interact with each other. Under this condition, the Schrödinger equation governing electron motion can be simplified as:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r) = E\psi(r) \quad (2)$$

Considering the temperature is at 0 K and based on the electron configuration within energy levels, the electron density can be determined as:

$$\rho = \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E_F^{\frac{3}{2}} \quad (3)$$

When further considering the attraction of the nucleus to electrons and the repulsion of electrons to electrons, if the energy is expressed in terms of electron density, it can be formulated as:

$$E_{TF}[\rho(r)] = C_F \int \rho(r)^{\frac{5}{3}} dr - Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|} dr_1 dr_2 \quad (4)$$

where the first term is the kinetic energy, the second term is the attraction of the nucleus to the electrons, and the last term is the repulsion between electrons. Notably, the expression is uniquely dependent on the electron density, which forms the foundational basis of the DFT method. Despite its simplicity, this model lacks consideration for exchange energy, leading to a slightly elevated total energy. Even with corrections, achieving high accuracy remains a challenge.

2.1.3 Thomas-Fermi-Dirac Model

In 1930, Dirac [54] refined and enhanced the Thomas-Fermi model by introducing the exchange energy functional term. This modification led to a revised expression for the total energy:

$$E_{TF}[\rho(r)] = C_F \int \rho(r)^{\frac{5}{3}} dr - Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|} dr_1 dr_2 - C_x \int \rho(r)^{\frac{4}{3}} dr \quad (5)$$

When describing the behavior of electrons within this expression, the model is still a free particle framework within a potential box while considering boundary conditions. However, practical application reveals that this approach falls short of achieving ideal performance. The expression for kinetic energy is the primary source of error, coupled with factors such as exchange energy error, resulting in low computational accuracy. To improve accuracy in calculations, the pursuit of more effective methods becomes imperative.

2.1.4 Hohenberg-Kohn-Theorem

The Hohenberg-Kohn theorem states that the external potential fields, $V(r)$ and N , can be replaced by the electron density $\rho(r)$ of the ground state in the electronic system, and $\rho(r)$ can be used as a new fundamental variable to determine the properties of the ground state of the system (regardless of the degeneracy state). This theorem mainly includes the first theorem and the second theorem [55].

The first theorem holds that: for an N particle system, there is a one-to-one correspondence between its ground state electron density $\rho(r)$ and the external potential $V(r)$, and the external potential $V(r)$ is uniquely determined by $\rho(r)$ (it may differ by a constant). This theorem preliminarily points out that it is feasible to replace the multi-electron wave function with the electron density distribution function, which can be used to determine the properties of the system.

The second theorem holds that: for any trial function $\rho(r)$, if it satisfies $\rho(r) \geq 0$, and also satisfies the condition $\int \rho(r) dr = N$, then $E_v[\rho(r)] \geq E_0$. Here, E_0 represents the ground state energy, and N represents the number of electrons in the system. Therefore, by knowing and minimizing the expression form of the energy functional $E[\rho]$ through variation, one can obtain the ground state electron density and energy level. The minimum value of the energy functional corresponds to the total energy of the system's ground state.

The Hohenberg-Kohn theorem, based on density functional theory, establishes that the ground state electron density of a system is uniquely determined and correlates with the ground state energy. However, for the theory to be effectively applied, an explicit expression of the functional $E[\rho]$ is required. This challenge was addressed by Kohn and Sham.

2.1.5 Kohn-Sham Equations

Hohenberg-Kohn Theorem [56] demonstrates the existence of the energy functional but doesn't provide a specific expression for it. The formulation of this expression is a crucial issue for practical calculations. In 1965, Kohn and Sham proposed a solution: the Kohn-Sham method. This method involves separating the main part of the total energy expression, namely the kinetic energy term (which is straightforward to handle due to the lack of interactions). Then, an approximation method is used to calculate the remaining part, fitting the electron

density function with the wave function of an imaginary non-interacting multi-fermion system. This process yields the Kohn-Sham equations:

$$[T_S + V_{eff}(r)]\psi_i(r) = \varepsilon_i\psi_i(r) \quad (6)$$

The expression of the effective potential $V_{eff}(r)$ can be expressed as:

$$V_{eff}(r) = V_{ne}(r) + \int \frac{\rho(r')}{|r-r'|} + \frac{\delta E_{XC}}{\delta \rho(r)} \quad (7)$$

Where the first term is the attraction potential of the nucleus, the second term is the Hartree potential between electrons, and the third term is the exchange-correlation potential (this term can be abbreviated as $V_{XC}(r)$).

The Kohn-Sham equation is considered more rigorous than the Hartree-Fock method because it accounts for the many-body problem rather than neglecting it. However, a significant challenge in density functional theory (DFT) lies in accurately addressing the exchange-correlation energy. This challenge involves obtaining an appropriate expression for the exchange-correlation functional [57].

2.1.6 Exchange-Correlation Functionals

The Kohn-Sham method has been a breakthrough in density functional theory, with the pursuit of reasonable exchange-correlation functionals being a primary focus of DFT development. The accuracy of the exchange-correlation energy directly impacts the precision achievable in calculations. Chemists have developed several effective methods to approximate exchange-correlation energies. Below are brief descriptions of several proposed approximation methods.

Local Density Approximation (LDA) [58]: the exchange-related functional term is approximated to depend uniquely on the local electron density. This approximation stems from the assumption that electrons outside the nucleus move rapidly, maintaining an approximately uniform density within small spatial volume elements. In mathematical terms, the exchange-related functional term can be expressed using the following formula:

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r)\varepsilon_{XC}[\rho(r)]dr \quad (8)$$

Logically, LDA should provide accurate results when applied to calculate a uniform electron gas system. However, in practice, it falls short of ideal performance. Typically, the calculated correlation energy tends to be higher than the accurate value, often approximately twice as much, leading to higher-than-expected bond energies. This discrepancy highlights the need for improved approximation methods with improved accuracy to minimize errors.

Generalized Gradient Approximation (GGA) [59]: It is believed that electron density is not uniformly distributed, indicating an error in describing it with a

uniform density. To rectify this, an electron density gradient is introduced to account for the non-uniformity of the distribution. This adjustment brings the calculation closer to the real situation of the system.

$$E_{XC}^{GGA}[\rho_{\omega 1}, \rho_{\omega 2}] = \int f[\rho_{\omega 1}, \rho_{\omega 2}, \nabla \rho_{\omega 1}, \nabla \rho_{\omega 2}] dr \quad (9)$$

Compared to LDA, GGA offers improved calculation results for both atomic correlation energy and exchange energy. However, it only marginally affects the ionization potential of valence shell electrons. Particularly for relatively light elements, the calculations of GGA generally align well with experimental data. Additionally, GGA has shown enhancements in the calculated values of energies associated with metallic bonds, covalent bonds, hydrogen bonds, and van der Waals interactions. Currently, there are numerous common GGA functional forms, including B88, PW86, PW91, PBE, and LYP [60–65].

2.1.7 Basis Sets

The Kohn-Sham equations describe the iterative computation of the single-electron orbitals $\{\psi_i\}$, yet the method does not prescribe the specific orbitals employed in numerical computations. Instead, these orbitals are typically expanded as linear combinations of basis set functions. Two commonly used types of basis sets are linear combinations of atomic orbitals (LCAO) and plane waves.

LCAO basis set expands orbitals using functions centered on the nuclei. The advantage of LCAO basis sets is their ability to model vacuum regions more easily, as there are no basis functions without nuclei, leading to the complete vanishing of the electron density. However, this also requires special attention at surfaces to ensure that the basis functions extend sufficiently into the vacuum.

Plane-wave basis sets are suitable for periodic systems due to the inherent periodicity of plane waves. This method is commonly implemented in software packages such as VASP [66]. The Bloch functions u_k are expanded using plane waves as

$$u_k = \sum_G \frac{a_{i,k,G}}{\sqrt{V}} \exp(iG \cdot r) \quad (10)$$

where $\{G\}$ are the reciprocal lattice vectors and $\{a_{i,k,G}\}$ are the plane wave coefficients. The kinetic energy of a plane wave is $\frac{\hbar^2}{2m}|k + G|^2$, and intuitively, plane waves with very large energies are unimportant and negligible. Therefore, the set of reciprocal lattice vectors considered at each k is truncated by introducing a cutoff for the kinetic energy. This ensures that only plane waves within the corresponding origin-centered sphere in reciprocal space are retained. The plane wave basis sets offer several advantages. Firstly, computing the Fourier transform is rapid, and multiple calculations can be efficiently performed in reciprocal space. Secondly, plane waves are orthonormal by construction, eliminating basis set

superposition error. Thirdly, a single parameter, the cutoff energy, can be adjusted to systematically improve convergence. However, the plane wave basis set has drawbacks. The charge density in vacuum regions does not vanish completely due to the absence of high-frequency components of the wave functions, and charge can accumulate on the vacuum side of potential barriers dropping below the Fermi level. Additionally, very large cutoff energies are required to represent core electrons, which is mitigated by using pseudopotentials.

2.1.8 Pseudopotentials

The pseudopotential method is based on the notion that core electrons are minimally affected by the chemical environment [67], allowing them to be approximated with wave functions that remain constant. This approach, known as the frozen core approximation, effectively reduces the number of plane waves required in core electron calculations. A pseudopotential replaces the electron density from a selected set of core electrons with a smoothed density tailored to match the physical and mathematical properties of the true ion core. These core electrons are then consistently represented in this approximation in all subsequent calculations. Modern DFT codes typically provide a library of pseudopotentials that includes an entry for most elements in the periodic table.

The details of a particular pseudopotential define a minimum energy cutoff required for calculations involving atoms associated with that pseudopotential. Pseudopotentials that demand high cutoff energies are considered ‘hard’, while those requiring lower cutoff energies are deemed ‘soft’, offering greater computational efficiency. One of the most widely used frozen core approaches is the projector augmented-wave (PAW) method, originally introduced by Blöchl [68]. In the PAW method, the relationship between valence wave functions and pseudo wave functions is established through a transformation operator. This enables the computation of properties associated with real wave functions without explicitly calculating these wave functions, resulting in enhanced computational efficiency.

2.2 Molecular Dynamics

Molecular dynamics (MD) simulation is a widely used method for studying large and complex systems. It involves simulating the movement of atomic nuclei using computers to gain insights into the structure and properties of the system. As computer technology advanced and simulation algorithms refined, MD simulations can extend to longer time scales, allowing the study of phenomena occurring over hundreds of nanoseconds or microseconds. However, despite these advancements, MD simulations still face significant challenges on longer time scales. Overcoming these challenges requires ongoing improvements in computer technology and the development of faster-supporting algorithms and innovative simulation methods.

Newton's laws of motion are foundational principles of MD simulations. This approach involves describing the evolution of molecular motion over time based on the principles of molecular mechanics, which states that the motion of an object is determined by the net force acting upon it. The classical trajectories of particles can be calculated by integrating the Newton's law of motion:

$$a_i = \frac{F_i}{m_i} = \frac{\partial^2 r_i}{\partial t^2}, i = 1, 2, \dots, N \quad (11)$$

Integrating the above equation over time allows us to predict the position and velocity of each particle within the time interval ∂t . This process is iterated continuously, leading to the determination of particle movement within the system at different times, and providing various information such as position, speed, and acceleration.

To obtain the motion states of particles in the system at different times, various integral methods are commonly used to solve Newton's equations of motion and acquire relevant information. Although the efficiency and accuracy of different methods may vary, they generally employ the finite difference method to integrate the second-order differential equation and obtain its solution. Commonly used methods include the Verlet method, the leapfrog algorithm, the Beeman method, and the Gear prediction-correction method. LAMMPS, for example, uses velocity-Verlet integrator, which has a local error on the position of the order of $O(\Delta t^4)$ and velocity $O(\Delta t^2)$.

The MD simulation is based on the following fundamental assumptions: approximation of effective potential and equivalence of ensemble average and time average in thermodynamic quantities. Under the premise of satisfying these assumptions, dynamic simulation is conducted by following these steps: selecting the size of the central unit cell, choosing the potential function, specifying the temperature and density of the system, determining the initial spatial distribution and velocity distribution, and finally establishing the time step and total number of simulation steps.

Efforts are made to simulate macroscopic systems with fewer particles due to the computational challenges posed by a large number of particles, even with modern supercomputers. To overcome this, periodic boundary conditions are employed. This approach involves constructing the simulated system by stacking basic units in different directions, retaining only the basic units during simulation while generating additional units by translating them. This ensures a constant number of particles in the system, aligning with practical computational constraints.

MD simulations are conducted within specific equilibrium ensembles: Micro-canonical ensemble (NVE) maintains a constant number, volume, and energy of atoms. Canonical ensemble (NVT) keeps the number of atoms, volume, and temperature constant, with the total dynamic force maintained at zero. Isothermal-isobaric ensemble (NPT) maintains constant pressure, temperature, and number of atoms. Isoenthalpic-isobaric ensemble (NPH) maintains a constant number of atoms, pressure, and enthalpy, making it suitable for scenarios involving volume

changes. During the actual application process, different ensembles can be selected based on specific requirements and objectives.

In MD, the analysis is limited to the motion of atom-like point masses, with no explicit consideration of electrons within the system. Forces acting on atoms originate from both surrounding electrons and the nuclei of neighboring atoms. To model these interactions, empirical potentials or force fields are employed. The forces acting on atoms are determined by empirical potentials and can be calculated using the following equation:

$$F_i = -\nabla_i U \quad (12)$$

The outcomes of MD simulations heavily rely on the empirical potential chosen for a particular system. Considering the unattainability of perfect empirical potentials, a compromise in accuracy becomes unavoidable.

2.3 Machine Learning-based Molecular Dynamics Simulations

Ab initio molecular dynamics is a highly accurate method that calculates atom and electron interactions fully quantum mechanically, typically using ab initio calculations like Density Functional Theory (DFT). However, this method often faces limitations in terms of the size of simulation cells and timescales. Force fields are employed to significantly accelerate such calculations. These force fields are parametrizations of potential energy, ranging from simple empirical functions to more complex functions derived from thousands of ab initio calculations. Manually Crafting accurate force fields is a time-consuming process that requires extensive expertise.

An alternative approach to reducing computational costs and human intervention is machine learning. In this method, the prediction of the target properties is based on automatic interpolation between known training systems previously calculated using ab initio methods. This streamlines the generation of force fields compared to classical force fields, which often require manual or empirical parameter adjustments. However, determining the proper minimal training data remains a challenge. One effective and automatic solution is on-the-fly learning, where an MD calculation is used to gather training data. During the MD run, ab initio data is selectively incorporated into the training set. A force field is continuously constructed from existing data, and at each step, the method decides whether to perform an ab initio calculation to update the force field or use the current and skip learning for the step. A probability model for error estimation, built from newly sampled data, plays a crucial role in this process. As the force field becomes more accurate, less sampling is required, reducing the need for expensive ab initio steps. This approach not only controls the convergence of the force field but also enables a comprehensive exploration of phase space for training structures.

The key to on-the-fly machine learning is the ability to predict force field errors on newly sampled structures without relying on ab initio calculations. To generate a machine-learning force field, several structure datasets are necessary. These datasets define the Bravais lattice, atomic positions, total energy, forces, and stress tensor calculated from first principles. Using these datasets, the machine learning model identifies local configurations and constructs an appropriate force field, with descriptors that capture radial and angular distributions of neighboring atoms around the given site.

This methodology ensures a more efficient and accurate way to generate force fields for molecular dynamics simulations, significantly accelerating the simulations while maintaining high accuracy. It also facilitates the study of complex systems over larger spatial and temporal scales than would be feasible with ab initio methods alone.

CHAPTER 3

RESULTS

3.1 Biased diffusion on Cu surfaces due to electric field gradients

3.1.1 General Concept

When a high electric field is applied on metal surfaces, it alters the diffusion dynamics of surface adatoms, causing field-induced biased surface diffusions and surface modifications [1–3]. This may lead to the growth of field-emitting nano-protrusions on metal surfaces, which is one of the most plausible mechanisms proposed to explain the occurrence of vacuum breakdown. The magnitudes of electric fields that can lead to vacuum breakdowns are typically in the range of dozens of GV/m [69], while in real experiments, only electric fields of a few hundred MV/m are applied [14], which are considered too low for initiating arcs. Therefore, there must be a feedback loop of self-reinforcing growth of surface protrusions [2,70], which can induce local field enhancement and ultimately result in subsequent vacuum breakdown. Due to the roughness of metal surfaces, a large number of protrusion spots can initiate such a feedback loop and damage the surface structures themselves. Unfortunately, achieving a desirable reduction in the occurrence of breakdowns is not feasible since their mechanisms remain completely unknown.

The process of protrusion growth is too fast to observe directly in experiments. However, with advancements in theoretical and computational technology, it becomes increasingly possible to understand the mechanisms governing surface protrusion growth. Tsong and Kellogg proposed a theory regarding biased atomic diffusion in the presence of an electric field gradient, where the diffusion is biased toward the direction of the strong electric field gradient [19]. This can be predicted by polarization characteristics (e.g. dipole moment and polarizability). Recently, Kyritsakis et. al. [31] have improved the theory by considering the charge redistribution of the entire surface based on a single jump of a migration adatom. The bias can be expressed as a migration energy barrier change ΔE_m :

$$\Delta E_m = -\mu_{sl}F_l - \frac{\alpha_{sl}}{2}F_l^2 - \mu_{sr}\Delta F - \alpha_{sr}F_l\Delta F \quad (13)$$

where F_l is the strength of the electric field at the initial lattice site of the atom, μ is the effective atomic dipole moment, and α is the effective atomic polarizability of the adatom. These two parameters are not only material-dependent, but also vary as a function of the local atomic environment of an adatom. In other words, they differ among surface orientations, or migration processes. The subscript sl denotes the difference between the lattice site and the saddle point, e.g. $\mu_{sl} \equiv \mu_s - \mu_l$ and $\alpha_{sl} \equiv \alpha_s - \alpha_l$, and sr denotes the difference between the saddle point

and the reference system (flat substrate surface with no adatom), e.g. $\mu_{sr} \equiv \mu_s - \mu_r$ and $\alpha_{sr} \equiv \alpha_s - \alpha_r$, $\Delta F \equiv F(x_s) - F(x_l) = \gamma(x_s - x_l)$.

3.1.2 The MD—FEM electrostatic models

We simulated the diffusion of Cu adatoms along a nanowire surface using molecular dynamics (MD) (LAMMPS), concurrently coupled with electrodynamics (FEMOCS code [30]). The thickness of the MD region was 8 interatomic distances (~ 20 Å) and 2 adatoms were added on the nanowire surface, with the wire radius ranging from 10 to 20 Å. The three lowest-index surfaces in terms of Miller indices, the $\{100\}$, the $\{110\}$, and the $\{111\}$ were studied, the cross-section of different surfaces are shown in Figure 1. To introduce the effect of electric fields, we modified the classical MD by coupling it to finite elements methods (FEM). The simulated system was extended with a continuous surface mesh beyond the 20 Å thick MD region, allowing for a more realistic calculation of the electric fields with the FEM.

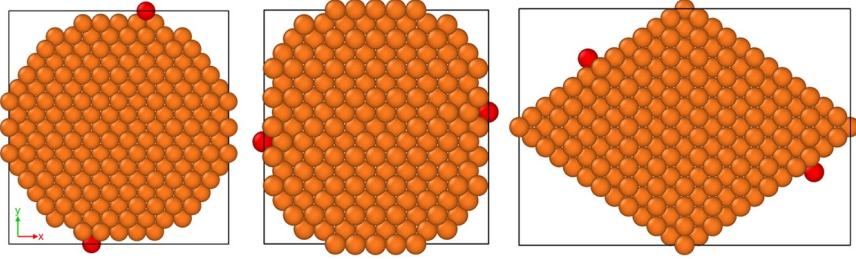


Figure 1: Cross section of the MD simulated nanowires, from left to right are $\{110\}$, $\{110\}$, and $\{111\}$, respectively. The adatoms are marked in red, while the rest of the atoms are marked in copper color.

The distribution of the electric field in our simulations was obtained by using the FEMOCS [30] library, which is a FEM solver. FEMOCS solves the electric field distribution around the metallic equipotential surface and calculates the surface charges. These charges are then distributed to surface atoms, resulting in electrostatic forces added within the MD algorithm. Figure 2 is the extended nanotip system. The MD region has periodic boundaries in the z-axis and open boundaries in the x-y plane, while the extended FEM simulation box has open boundaries in the z-axis and periodic boundaries in the x-y plane.

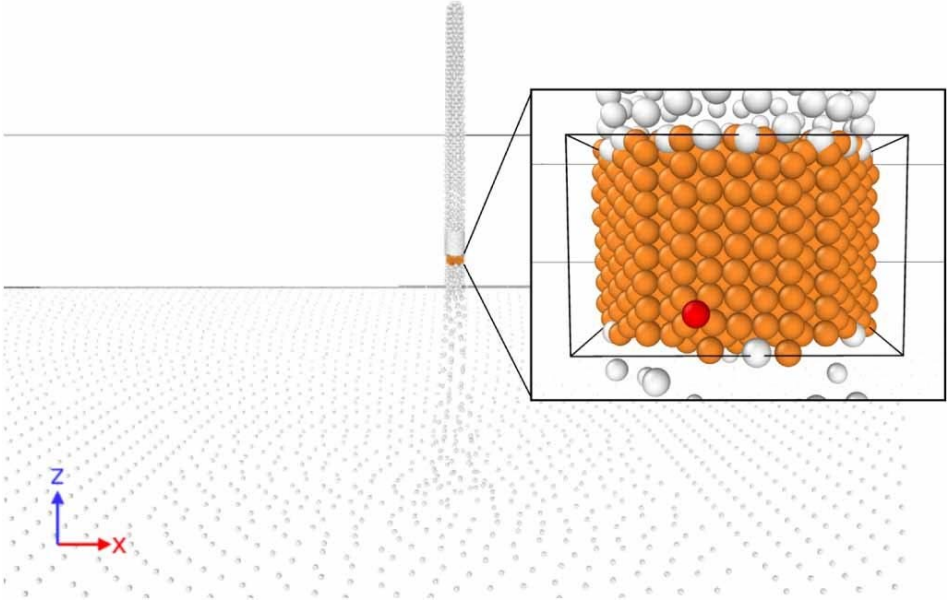


Figure 2: Extended simulation system, the MD region is copper-colored (zoomed into in the inset), and the static and continuous FEM extension region is in gray. The system has periodic boundaries in the x-y plane, and open boundaries in the z-axis. The MD region has its z-span, independently of the FEM extension.

The electric fields and the electrostatic potentials of the MD region in different extended structures are shown in Figure 3. We used two different nanotip structures: a 93 nm tall tip and a shorter 5 nm one, each with a similar cross-sectional shape to that of the MD region. For the nearly elliptical $\{100\}$ nanowire, an elliptical extension cross-section was used; for the more flattened $\{110\}$ wire, a similar flattening extension cross-section was applied; and for the $\{111\}$ wire, a diamond-shaped was used to the extension cross-section. The MD region was positioned either at the bottom, middle, or top of the tall nanotip or in the middle of the short one.

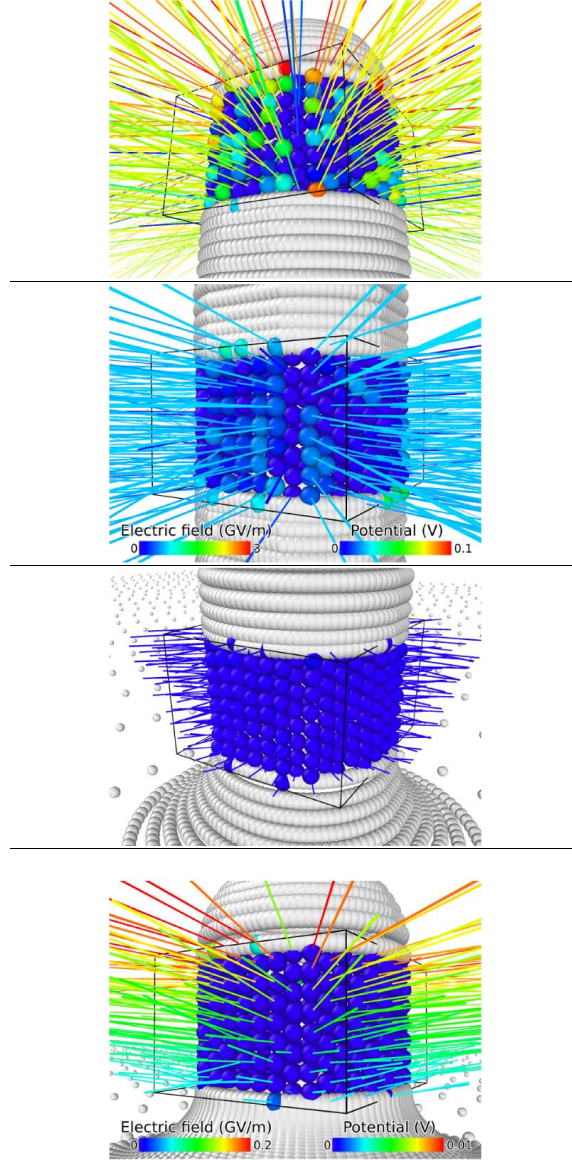


Figure 3: The electric fields and electrostatic potential on the $\{1\ 0\ 0\}$ surface with an external electric field of 100 MV/m. The top three panels represent the tall nanotip (93 nm), while the bottom panel is the short nanotip (5 nm). The field vectors point toward the surface atoms, although the arrowheads are not visible. Atoms are color-coded according to their potential, while the field vectors are colored according to their magnitude. In the top three panels, the scales of the potential and the field vectors are consistent to highlight how the absolute value of the field increases in the tall nanotip. The magnitudes are scaled up in the bottom-most panel to ensure better visibility of the field vectors and the potential coloring.

3.1.3 The DFT models

To calculate the polarization characteristics of single adatoms placed on Cu surfaces of three different Miller indices, I performed simulations using the Vienna Ab Initio Simulation Package (VASP) along with its corresponding pseudopotential database [66,71,72]. I used the projector-augmented wave (PAW) method [68,73] in conjunction with the PBE functional to describe the electronic exchange and correlation effects [63]. A $4 \times 4 \times 1$ K-point mesh was used to sample the Brillouin zone following the Monkhorst-Pack scheme [74]. This mesh satisfies $N_k \cdot a \geq 35 \text{ \AA}$ for x, y, and z directions, where N_k is the number of K-point samples and a is the simulation box size at a given direction. The cut-off energy was set to 600 eV, and the structures were relaxed until the residual forces were less than $0.01 \text{ eV \AA}^{-1}$. A vacuum space of at least 25 $\text{\AA}$ was added and dipole corrections were applied between the slabs.

Three different Cu slabs were simulated, one for each of the simulated surfaces, as shown in Figure 4. The slab thicknesses were 6, 8, and 8 monoatomic layers for the $\{100\}$, $\{110\}$, and $\{111\}$ systems, respectively. An adatom was positioned on the top surface of each slab. To determine the saddle point for the hopping barrier in the $\{100\}$ and $\{110\}$ surfaces, I followed the same symmetry considerations as outlined in [31], where the adatom was fixed with respect to the x-y plane at the bridge site while allowing it to relax along the z-axis. However, obtaining the saddle point for the $\{111\}$ surface is more complex due to an intermediate local minimum that would occur at the hcp site [29]. Since our focus in this work is only on comparing the polarization characteristics of adatoms deduced from MD and DFT simulations, we can approximate these characteristics on the $\{111\}$ surface with a good level of confidence by their values at the lattice site.

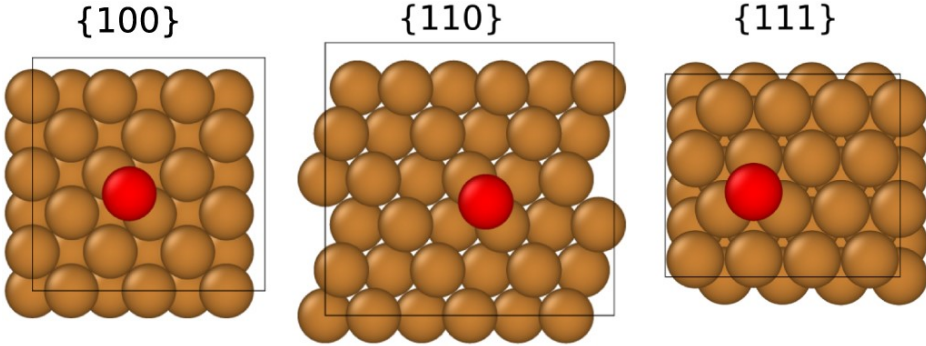


Figure 4: The unit cells of the three different surface systems $\{100\}$, $\{110\}$, $\{111\}$ with added adatoms simulated by DFT.

3.1.4 Drift of Cu adatoms under inhomogeneous electric fields using MD-FEM

To study the drift of single adatoms along the z-axis, we collected the evolution of the average z-axis of the adatoms on different surfaces, as shown in Figure 5. The different jump rates are evident: on the $\{1\ 0\ 0\}$ surface, individual jumps appear in the average z-axis despite the lengthy time scale, while on the other two surfaces, the jumps seem to blend. We observed that in $\{1\ 1\ 0\}$ and $\{1\ 1\ 1\}$ surface simulations, it was necessary to track all atoms from the surface layer, not just the adatoms initially placed on these surfaces. This is because many transitions on $\{1\ 1\ 0\}$ and $\{1\ 1\ 1\}$ surfaces occur via exchange events: the diffusing adatom occupies a neighboring lattice site temporarily freed up due to thermal vibrations. The adatom becomes trapped and transforms into a regular surface atom, while the freed-up atom continues to migrate on the surface until the next exchange event occurs. Such exchange events primarily impact diffusion on the $\{1\ 1\ 0\}$ surfaces, as hopping diffusion is very rapid on the close-packed $\{1\ 1\ 1\}$ surface. It is worth noting that the linear increase of the z-axis in the $\{1\ 1\ 1\}$ surface (Figure 5c) indicates the strongest bias effect of the electric field gradient on diffusional hopping of adatoms between the lattice sites on this surface. Three lines that diverge from the overall trend represent the simulations where the two adatoms formed a dimer and continued diffusion with a lower bias.

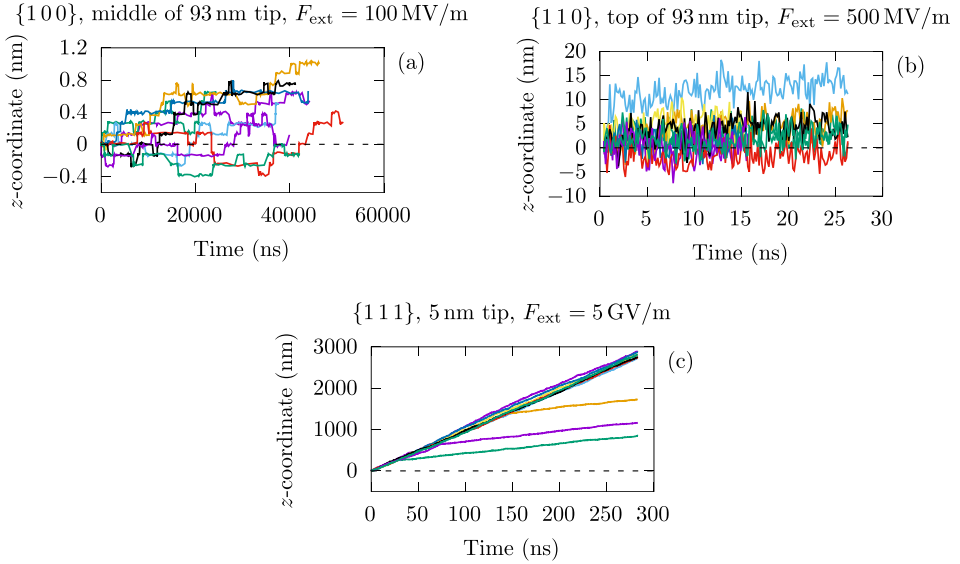


Figure 5: Evolution of the average z-axis of two adatoms diffusing on different surfaces with different electric fields: Panel (a) displays all 10 runs on the $\{1\ 0\ 0\}$ surface in the middle of the 93 nm nanotip, under an applied field of 100 MV/m. Panel (b) illustrates the same on the $\{1\ 1\ 0\}$ surface at the top of the nanotip, with a field of 1 GV/m. Panel (c) presents the $\{1\ 1\ 1\}$ surface of the 5 nm nanotip, with a field of 5 GV/m.

In Figure 6 we show the drift velocity as a function of the electric field gradient γ . The drift velocity is calculated as the z-coordinate of adatoms at the end of the simulation divided by the simulation time. The obtained velocities are averaged over ten repetitions in each case. The top three rows exhibit outcomes for the 93 nm tall nanotip. These diffusion processes were simulated at various segments of the tip: the top, middle, and bottom, presented from top to bottom. The final row displays the shorter 5 nm nanotip. Results are organized in columns as well, with the drift velocity for surface diffusion on the $\{100\}$, $\{110\}$, and $\{111\}$ surfaces presented from left to right.

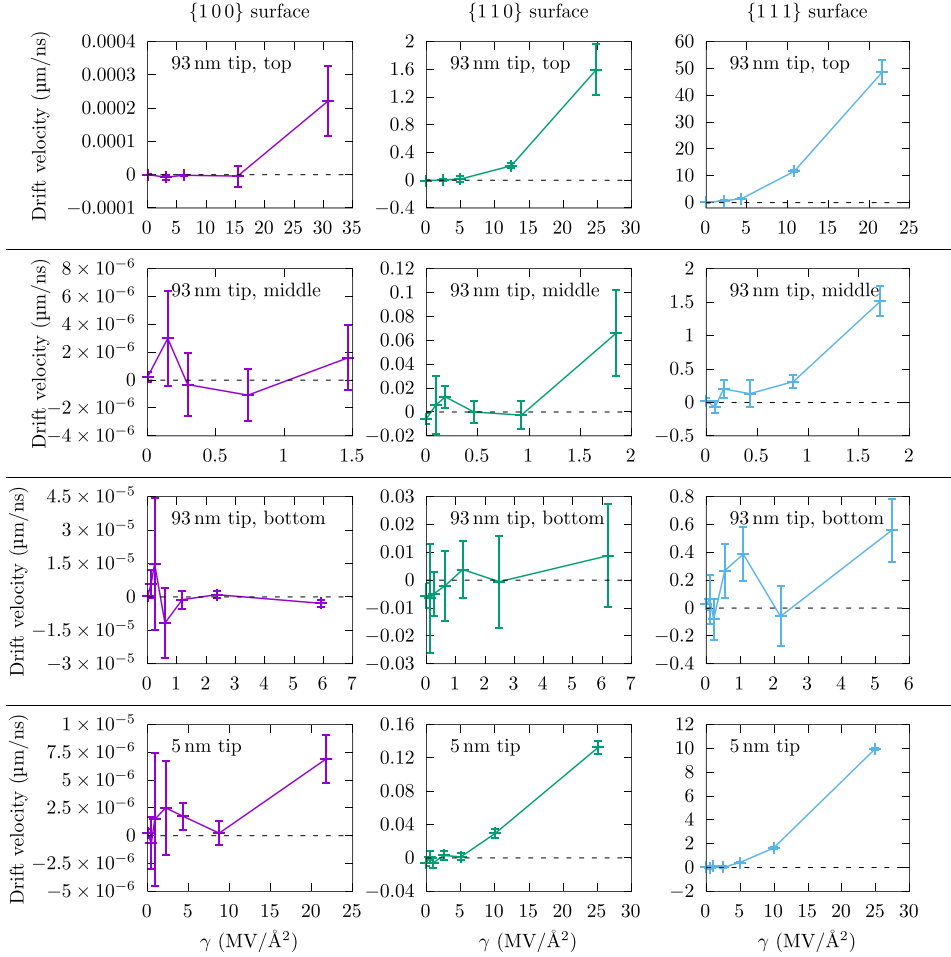


Figure 6: Average surface diffusion drift velocity in different geometries and on different surfaces. Error bars are one standard deviation. Note that also the local electric field F varies linearly with the gradient in each plot.

3.1.5 The comparison of polarization characteristics between MD-FEM and DFT

We estimated the effective dipole moment μ and polarizability α that are consistent with the observed biased diffusion characteristics calculated by the MD-FEM method and compared them to the corresponding values calculated directly from DFT calculations. The polarization characteristics of diffusing adatoms were deduced from the DFT calculations following the methodology developed previously in [31]. For each cell in Figure 4, we performed calculations for five different values of the electric fields within the range from -2 GV/m to +2 GV/m. From these calculations, we extracted the effective dipole moment μ_s (μ_l for the $\{1\ 1\ 1\}$ surface) and polarizability α_s (α_l for the $\{1\ 1\ 1\}$ surface) by fitting a parabola to the corresponding field-energy curve, as prescribed in [31]. Additionally, we calculated the reference values μ_r and α_r for all the surfaces with no adatoms present.

In the MD-FEM method, we estimated polarization characteristics from the diffusion bias, which can be attributed to the modification of the migration energy barriers by the electric field and its gradient. The unbiased ($\gamma = 0$) jump rate Γ is defined by the Arrhenius equation:

$$\Gamma = \nu \exp\left(-\frac{E_m - u_{sl}F - \frac{\alpha_{sl}F^2}{2}}{k_B T}\right) \quad (14)$$

where ν is the attempt frequency, E_m is the migration energy barrier in the absence of applied field. The expected displacement $\langle x \rangle_b$ of the biased diffusion after time τ is

$$\langle x \rangle_b = 2\tau l \Gamma \sinh\left(l\gamma \frac{u_{sr} + \alpha_{sr}F}{k_B T}\right) \quad (15)$$

The mean displacement is proportional to the unbiased jump rate Γ and depends on the polarization characteristics of the surface. This estimation can be done independently of the migration rate Γ and the simulation time, dividing by the mean square displacement $\langle x^2 \rangle = \tau l^2 \Gamma$

$$\frac{\langle x_b \rangle}{\langle x^2 \rangle} = \frac{2}{l} \sinh\left(l\gamma \frac{u_{sr} + \alpha_{sr}F}{2k_B T}\right) \quad (16)$$

We can estimate u_{sr} and α_{sr} on each surface by fitting equation (16) to the observed $\frac{\langle x_b \rangle}{\langle x^2 \rangle}$ at each (F, γ) point. The dipole moment μ_{sr} and the polarizability α_{sr} on three different surfaces are shown in Table 1. The results for the $\{100\}$ surface obtained from MD cannot reproduce the values from DFT, while the agreement of these parameters is qualitatively compared to the $\{110\}$ and $\{111\}$ surfaces.

Table 1: The dipole moment μ_{sr} and the polarizability α_{sr} on different surfaces.

Surface	μ_{sr}		α_{sr}	
	MD	DFT	MD	DFT
{100}	.0 $\pm$.2	.106 $\pm$.003	.1 $\pm$.1	.27 $\pm$.02
{110}	-.008 $\pm$.005	.094 $\pm$.006	.034 $\pm$.008	.30 $\pm$.04
{111} ^a	-.016 $\pm$.006	.162 $\pm$.003	.02 $\pm$.01	.23 $\pm$.02

^a The saddle point value for {111} surface is approximated by the value at lattice position (μ_{lr}, α_{lr}).

3.2 Polarization characteristics of Cu nano-particles due to high electric fields

3.2.1 General Concept

Tsong and Kellogg [19,22,23] proposed a formula to describe the biased diffusion of an adatom on metal surfaces with non-uniform fields, providing a strong qualitative understanding of how the migration barriers and the binding energies are modified by the fields based on the atomic polarization characteristics. Kyrtsakis et al. [31,32] discovered that their formula lacked rigor for a non-isolated adatom interacting with and sharing its charge with neighboring surface atoms. Subsequently, they developed a complete theory that incorporates the entire charge redistribution on the surface, ensuring the precise definition of relevant effective atomic dipole characteristics.

Considering the effects of an applied field on the diffusion of an adatom on metal surfaces, the total dipole moment p of a system of atoms under an electric field F can be expressed as [19]

$$p(F) = \mu + \alpha F + O(F^2) \quad (17)$$

where μ is the permanent surface-induced dipole moment and α is the polarizability. The total energy U under high electric fields can be given in terms of μ and α as [19]

$$U = U_0 - \mu F - \frac{1}{2} \alpha F^2 + O(F^3) \quad (18)$$

where U_0 is the total energy in the absence of an external field. The developed theory proposed by Kyrtsakis et. al. [31,32] has been successful in describing the polarization characteristics and the biased diffusion dynamics by disregarding higher orders $O(F^2)$ and $O(F^3)$ (also known as hyperpolarizability terms). The validity of this theory has been tested only for low fields up to 3 GV/m, due to computational limitations of the plane-wave-based DFT basis sets. The Vienna ab initio simulation package (VASP), the DFT package used in the literature, performs accurate calculations when electric fields range from 0 to ± 3 GV/m.

However, beyond this range, electrons tunnel through the surface barrier when the applied field is larger than 3 GV/m, leading to an unreliable result. Hence, it is not clear what field range for which higher-order terms $O(F^2)$, $O(F^3)$ can be neglected. I shall investigate whether this theory is valid for higher field strengths as well, which are relevant for vacuum breakdown and intense field emission as well.

The Gaussian package can handle DFT calculations for high fields up to 15 GV/m based on localized basis wavefunctions. This basis is commonly used for non-periodic, isolated structures, rather than the periodic slab models typically employed for atomic polarization characteristics, which are more representative of the interaction of high fields with large-scale metal surfaces. Here, our interest lies in testing the general behavior of such characteristics of metal surfaces exposed to high electric fields. Thus, I simulate various Cu nanoparticles to reveal these general characteristics while remaining suitable for the localized basis set of Gaussian package, then investigate the behavior of different Cu nanoparticles under high electric fields up to 15 GV/m to verify the validity of neglecting hyperpolarizability terms. The objective is to compare the total energy of the nanoparticles under electric fields as calculated by density functional theory (DFT) and by the polarization characteristics formula.

3.2.2 The structural modifications of Cu nanoparticles due to electric fields

In Figure 7, there are four different types of Cu nanoparticle structures, namely a simple atomic dimer (a, e), a 14-atom cube (b, f), two stacked 23-atom cubes (c, g), and three stacked 32-atom cubes (d, h), with Cu atoms positioned at the corners and centers of the faces in the FCC positions. Initially, I relaxed the structures without applying a field using the Gaussian DFT simulation package. The relaxed structures are depicted on the left-hand side (a-d) of Figure 7. To illustrate the impact of a high electric field on the dynamics of these atomic structures, I applied a strong electric field in the upward (+z) direction and relaxed the structures under its influence, as depicted on the right-hand side (e-h) of Figure 7.

In the case of the Cu atom dimer, I observed an increase in bond length (minimum energy distance) from 2.2 Å at zero field to 2.4 Å at a field strength of 15 GV/m. For the single-cube nanoparticle (NP), bond lengths along the direction of the applied field (the vertical axis) elongate by approximately 9%, while those perpendicular to the field direction (the horizontal axis) shorten by about 1%, inducing tetragonal distortion in the cube. When considering the 2-cube NP, even a field as low as 2 GV/m causes significant structural deformation, leading to the upward movement of atoms at the corners and bending of the entire NP structure, as depicted in Figure 7g. Similarly, for the 3-cube NP, a mere 1 GV/m field is adequate to trigger complete reconstruction, as illustrated in Figure 7h. This reconstruction involves compactification along the horizontal axis and stretching

along the vertical axis. Notably, the Cu atoms at the center of the top face, corresponding to ideal FCC positions, move upward along the $+z$ axis, while those at the corners shift toward the center to reach the energy minimum.

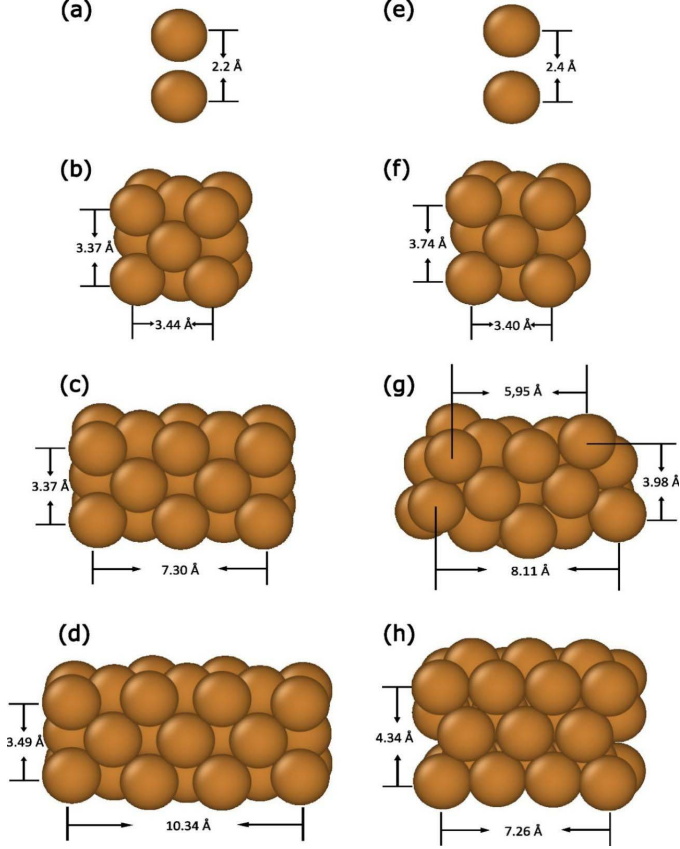


Figure 7: From top to bottom, side views of Cu dimer (a, e), single cube NP (b, f), two stacked cubes NP (c, g), and three stacked cubes NP (d, h), respectively. Solid lines denote bond lengths. Structures (a), (b), (c), and (d) are relaxed without an applied field, while (e) and (f) are relaxed under a 15 GV/m applied field, (g) under a 2 GV/m field, and (h) under 1 GV/m. In all cases, the field is applied vertically along the positive z -axis.

3.2.3 The effect of hyperpolarizability terms at extremely high electric fields

To investigate the effect of higher orders $O(F^2)$ and $O(F^3)$ terms at extremely high fields, I combine two DFT calculation approaches and packages (GAUSSIAN and VASP), as depicted schematically in Figure 8. Each relaxed structure of Figure 7 is analyzed as follows: I initially use GAUSSIAN to directly calculate the total energy of a given atomic system for fields up to 15 GV/m, then fit a parabola through them to determine the optimum values for μ , α , according to

Eq. (18), which reproduce the calculated energy values. To explore different computational approaches, I use VASP to calculate the parameters μ and α from low-field ($<3\text{GV/m}$) simulations as well, then substitute the obtained μ and α values from Eq. (17) into Eq. (18) to derive the total field-induced energy across the entire field range, while neglecting hyperpolarizability terms. Finally, I compare the energy-field curves obtained by three different methods to validate the more general, scalable, and computationally efficient method of Eq. (18). Note that maintaining fixed atomic positions throughout the field increment steps ensures the validity of extracting μ and α for each method and guarantees comparability among the three different evaluation methods. This consistency in atomic positions is important because the total energy U , U' , U'' , coefficients μ and α are uniquely dependent on the atomic positions. By keeping the atomic positions constant, the variations observed in the calculated parameters can be attributed to the changes in the applied field.

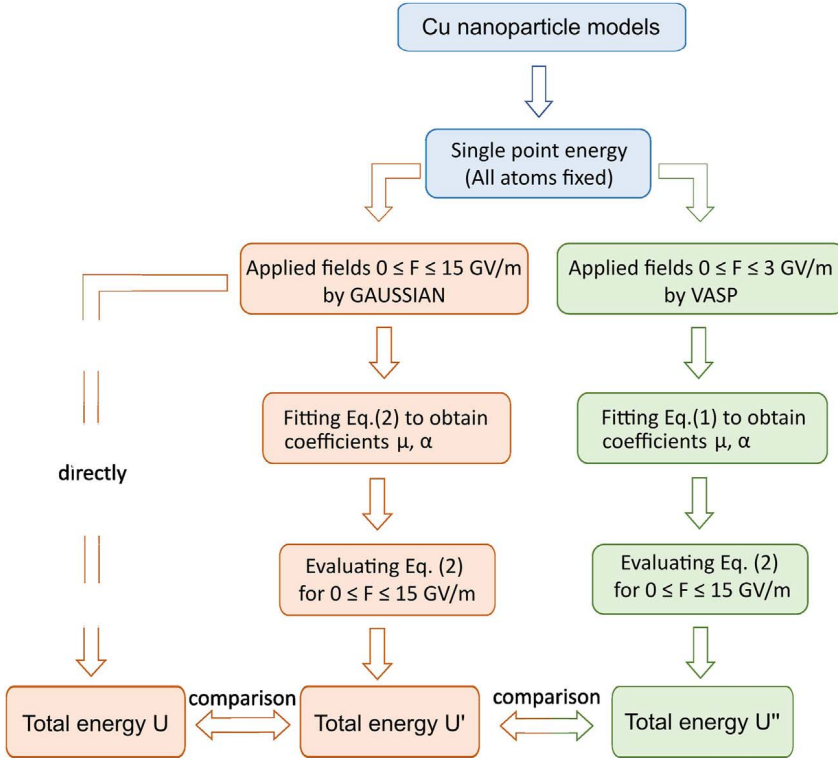


Figure 8: The workflow to illustrate the procedures of Cu nanoparticle simulations.

In Figure 9, I plot the field-induced energy of all simulated structures as a function of the applied field. The results from the three evaluation methods are presented. The total energies obtained from direct GAUSSIAN calculations (U) are represented by dots, while the curves derived from eq. (18) without considering hyper-polarizability terms are given by lines, with dashed lines corresponding to

μ, α calculated by fitting the parabolic energy curve obtained from GAUSSIAN (i.e. U' of Figure 8) and solid lines representing μ, α values calculated by using VASP (i.e. U'' of Figure 8).

If the hyperpolarizability terms are negligible, the total energies U, U', U'' should exhibit good agreement with increasing applied field. I observe that the U values perfectly follow the U' parabolic curve, indicating the insignificance of hyperpolarizability terms within the <15 GV/m field range. Additionally, the U'' values closely follow the U and U' values for applied fields less than 12 GV/m, with minor deviations for higher field strengths (>12 GV/m). These deviations are likely due to differences in the calculated polarization characteristics, as the two methods use different accuracies and DFT calculations with different basis sets.

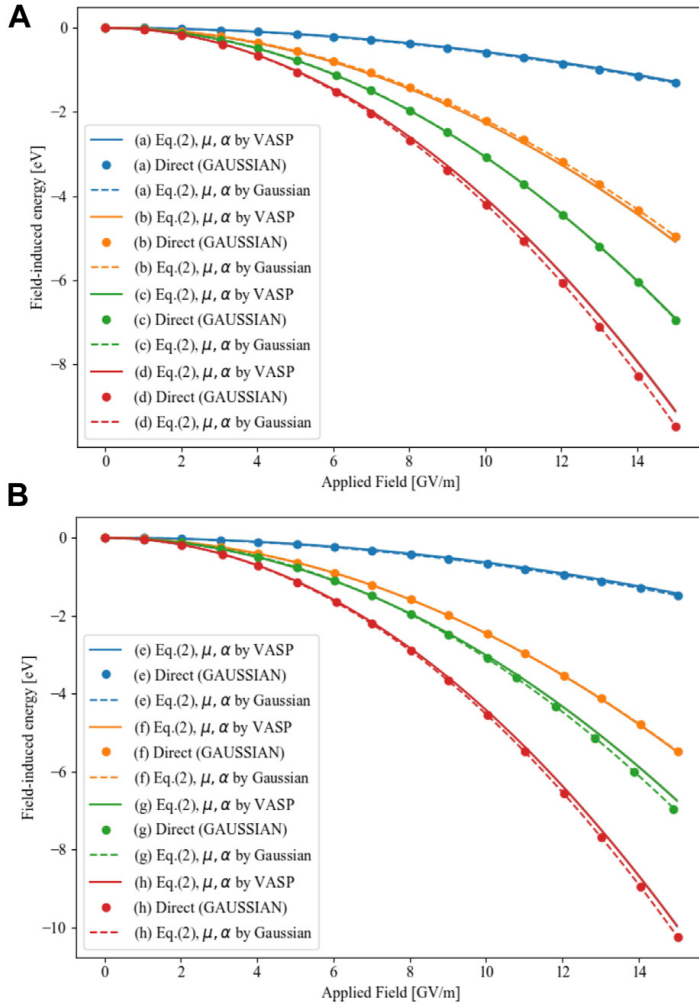


Figure 9: The field-induced energy of all simulated structures as a function of the applied field, all of which correspond to the labels of Figure 7.

Table 2 summarizes the values of μ and α obtained from two different methods and using two different DFT packages. The left-hand side columns display the μ and α values derived from VASP by fitting the dipole equation (17), while the right-hand side columns present the corresponding values obtained by fitting the energy equation (18) using GAUSSIAN total energies. Structures (a), (b), (c), and (d) exhibit zero permanent dipole moments due to their symmetry. However, after relaxation under fields, structures (f), (g), and (h) lose their symmetry, resulting in non-zero permanent dipole moments. The error margin for all values corresponds to the square root of the corresponding element of the curve fitting covariance matrix.

Table 2: The dipole moment μ and polarizability α of different NP structures as obtained from VASP by fitting the dipole equation (17) are listed as on the left-hand side columns, while the corresponding values by fitting energy equation (18) from GAUSSIAN total energies are given in the right-hand side columns.

Structure	μ [eÅ]		α [eÅV ⁻¹]	
	Eq. (1) – VASP	Eq. (2) – Gaussian	Eq. (1) – VASP	Eq. (2) – Gaussian
a	0.001±0.002	0.033±0.005	1.14±0.01	1.13±0.01
b	−0.001±0.002	0.022±0.004	4.52±0.01	4.43±0.00
c	−0.002±0.002	0.048±0.020	6.14±0.01	6.21±0.03
d	−0.003±0.003	0.079±0.009	8.09±0.02	8.50±0.01
e	0.001±0.001	0.044±0.001	1.27±0.00	1.26±0.01
f	−0.047±0.001	−0.069±0.000	4.82±0.01	4.77±0.00
g	−0.057±0.002	0.147±0.026	5.92±0.01	6.42±0.03
h	−0.016±0.003	0.059±0.012	8.87±0.01	9.16±0.02

3.2.4 The impact of the electric fields on the potential energy landscape

To explore the impact of the field on the potential energy landscape, Figure 10 displays the total energy of the Cu dimer plotted against the interatomic distance for three different field strengths (0, 8 GV/m, and 15 GV/m, the bond length elongates from 1.5 Å to 4.0 Å. The energy of the Cu dimer with a 1.5 Å bond length in the absence of an applied field serves as the reference point (0 eV), with other values presented as relative energies. It is evident that the potential well, represented by the energy minimum, gradually diminishes as the field strength increases, particularly for F=15 GV/m. This alteration in the equilibrium bond length of the Cu dimer, from 2.2 Å without a field to 2.4 Å when exposed to a 15 GV/m field, signifies a significant change in the potential energy landscape. Additionally, the strong agreement between the two calculation methods, even for F=15 GV/m (blue curve), highlights the reliability of the computationally efficient and scalable approach based on VASP for determining the potential

energy landscape. Finally, we see that the potential well, i.e., the minimum of the curves gradually disappears with the field increased up for $F = 15$ GV/m.

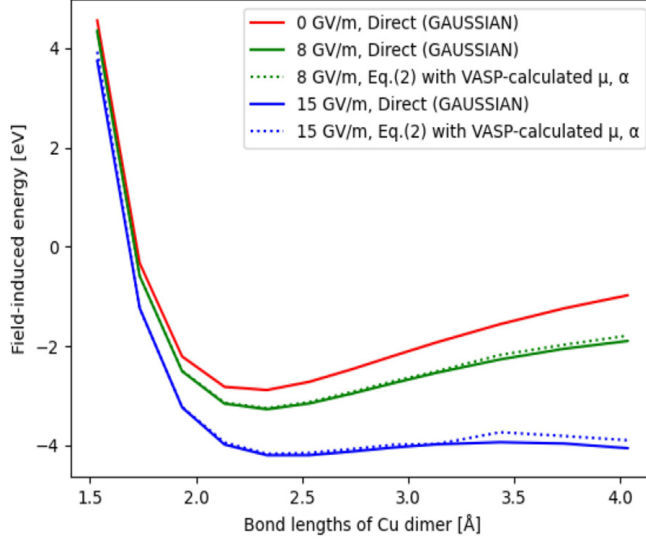


Figure 10: Total energy of Cu dimer as a function of the interatomic distance ranging from 1.5 Å to 4.0 Å. Solid curves are obtained from GAUSSIAN calculations, while dash curves are obtained by evaluating eq. (18) using VASP-calculated μ , α .

3.3 Field-induced surface restructuring on carburized tungsten structure — the R(15×12) reconstruction

3.3.1 General concept of carburized tungsten structure

When clean tungsten is annealed at high temperatures (typically between 2300 K to 2600 K) in a carbon-rich environment, carbon atoms diffuse to W{110} surfaces, leading to the formation of two particular types of surface reconstructions, i.e. the R(15×3) and the R(15×12), which exhibit specific periodicities on their atomic structure. Bertolini et. al [33] measured a 0.4 eV work function change when the R(15×12) reconstruction is exposed to a high electric field, suggesting a possible electric field-induced atomic structure modifications — surface restructuring. Such findings hold promise for gaining valuable insights into electric-field-induced surface.

However, the absence of the exact atomic structures of the R(15×12) reconstruction limits the potential to understand their properties and explore novel functionalities, creating an increasing need to find their exact atomic structures. To address this, Kim et al. [41,75] used extremely precise STM imaging in conjunction with DFT calculations to show that the R(15×3) reconstruction is formed by two hexagonal monoatomic layers of α -W₂C (one C and one W layer) on the W(110) surface. This structure was used as a basis block for proposing a model

for the R(15×12) surface. By closely examining STM images with near-atomic resolution, they suggested that the R(15×12) structure is formed by the two consecutive two R(15×3) cells, named “A-blocks”, followed by a 15×6 clean W(110) square area, designated as “B-block”. Unlike the R(15×3) reconstruction, there have been no DFT calculations confirming this hypothesis for the R(15×12) reconstruction. To understand the cause of the observed work function change on the R(15×12) surface, I initially conducted DFT calculations on the A-A-B atomic structure model. However, our findings revealed that this model is not compatible with the experimental STM observations. Consequently, I propose a complete new atomic structure for the R(15×12) surface, which closely reproduces the most characteristic features of the experimental STM images. Based on this new structure, our next step is to investigate how surface restructuring is induced by high electric fields.

3.3.2 Testing the state-of-the-art model of the R(15×12) reconstruction

The state-of-the-art hypothesis was proposed by Kim et. al. [75], yet no further DFT calculations have confirmed their hypothesis. I used DFT calculations to test their proposed atomic structure of the R(15×12) reconstruction, as shown in Figure 11a. According to their hypothesis, I constructed a unit cell consisting of a repeated slab with a 5×12 surface supercell. The W(110) substrate consists of five monoatomic layers aligned with the x-y plane. In the A-blocks, two monoatomic layers of hexagonal α -W₂C (0001) were placed on top of the W(110) substrate, with one layer of C atoms followed by one layer of W atoms. The B-block consists of one clean monoatomic W(110) layer placed on top of the substrate. I calculated the corresponding STM images in the constant-current mode using the Tersoff-Hamann approximation [76]. The resulting image along with the relaxed atomic structure is shown in Figure 11b.

I observed that the carbon-free B-block appears much darker in the simulated STM image than in the experimental one. Additionally, the carbon-rich A-blocks with hexagonal α -W₂C structures fail to reproduce the characteristic bright spots observed in the experimental STM image. The simulated STM image bears little resemblance to the experimental one. Furthermore, the atomic positions do not nest well with those expected based on the clear bright spots observed in the experimental STM image. Consequently, our DFT results confirm that the model proposed by Kim et al. cannot effectively reproduce the observed features of the R(15×12) surface.

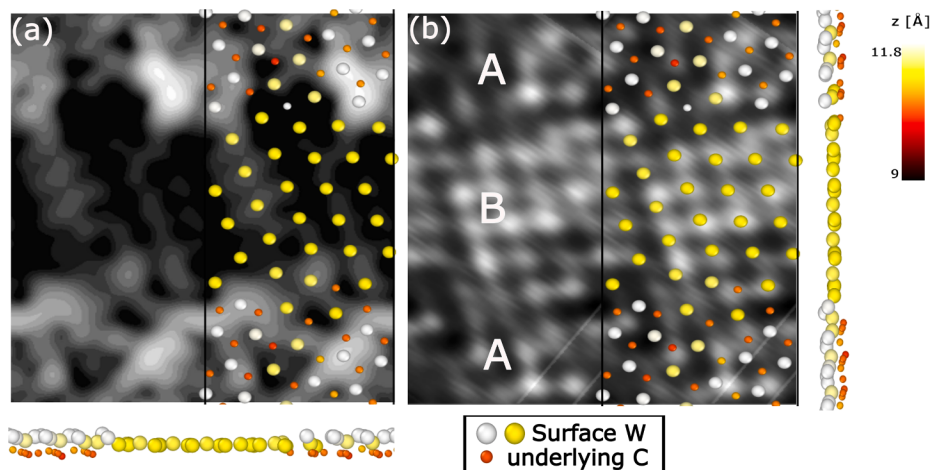


Figure 11: (a) The simulated constant-current STM image of the relaxed structure at sample bias of + 0.25V. (b) The experimental STM image with atomic resolution. In both images two periodic cells are shown with the atomic structure of the most top W layer and subsurface C layer being overlaid on them. The color coding corresponds to the z-coordinate of the atoms (height).

3.3.3 Analysis of the atomic-resolved experimental STM image

A closer examination of Figure 11b exhibits several very pronounced bright spots, suggesting that the surface coincides with the lattices of W(110). To investigate this suggestion further, we superimpose meshes corresponding to W(110) over the experimental STM image in Figure 12 as blue lines, while green lines divide the structure into two A-blocks and one B-block. We observe that most bright protrusions do nestle well within the W(110) grid cells, indicating that the top layer of the R(15×12) structure follows the W(110) lattice. This strongly contradicts the previous hypothesis that the A-block follows the hexagonal α -W₂C (0001) lattice.

This leaves a challenge, as the surface W atoms still need to maintain in the W(110)-type lattice structure even in the presence of sub-surface C layer. We observe that bright protrusions align perfectly with the W(110) lattice positions in the experimental STM image, indicating in certain cases, the W(110)-type structure remains intact regardless of the deposition of interstitial carbon atoms.

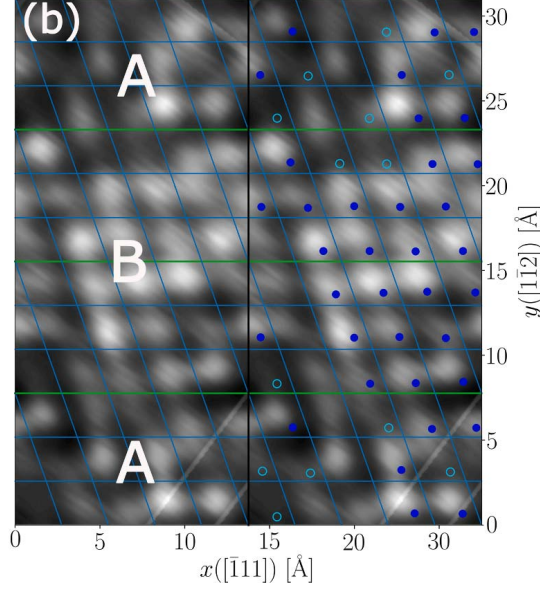


Figure 12: Atom-resolved experimental STM image of the R(15 $\times$ 12) surface by Kim et. al. [75], the image was superimposed by the mesh of W(110). The W(110) grid is shown in blue lines, while the green lines split it into two A-blocks and one B-block. The solid blue dots mark grid cells with bright protrusions and hollow cyan dots the ones with dark depressions.

3.3.4 Machine Learning potential for W-C

Simulating the R(15 $\times$ 12) surface reconstruction with DFT is extremely computationally expensive due to its very large unit cell. To overcome this challenge, we developed a machine-learning potential (force field) using VASP built-in machine learning module, which contains on-the-fly machine learning algorithms. To ensure the reliability of the trained machine-learning potential for more general W(110) surfaces with sub-surface C atoms, we ran DFT-MD simulations on different systems, illustrated in the inset of Figure 13. After performing 1000 MD steps while ramping the temperature within the NPT ensemble from 0 to 2500 K, we calculated the system energy for each step using our machine learning potential and compared it with the corresponding DFT values.

The resulting plot in Figure 13 demonstrates good agreements between DFT and the machine learning potential, with an RMS error of 0.043%.

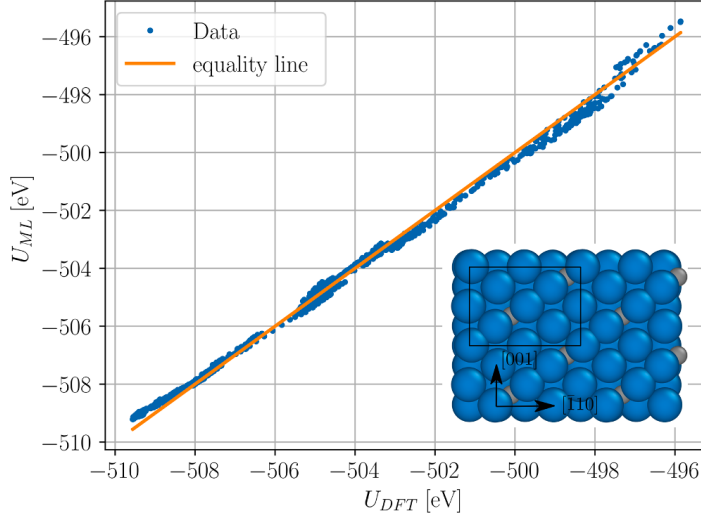


Figure 13: Potential energy of various steps of an MD simulation as predicted by DFT and our machine-learning potential. The inset shows the simulated 5-layer W(110) slab system, with blue atoms representing W and grey ones representing C. The unit cell of the system designated by the black box contains 40 W and 2 C atoms.

3.3.5 Finding the atomic structure of the R(15×12) surface

Before starting an extensive search for the optimal structures, we must first validate the hypothesis that the underlying carbon atoms are located right beneath the surface layer. To accomplish this, I performed DFT calculations on carburized tungsten systems, where carbon atoms were deposited beneath different tungsten layers. Figure 14a depicts the side view of the simulated structures, while Figure 14b illustrates the corresponding total energies. Our findings indicate that the structure depicted first in Figure 14a has the lowest energy, thereby confirming that the underlying C-layer is indeed deposited as the subsurface layer.

To find the atomic structure, I initially studied the energetically favorable structure for a sub-surface layer of interstitial carbon atoms on a pure W(110) surface. I performed simulations to analyze the relaxation of a smaller R(15×3) unit cell, containing a complete sub-surface layer comprising 15 carbon atoms. Our findings revealed that the carbon atoms relax at the interstitial sites, as shown in Figure 15a. Subsequently, upon the removal of two carbon atoms, the surface relaxed into the structure shown in Figure 15b. It is important to note that the tungsten atoms, corresponding to the grid cells where the sub-surface carbon atoms are absent, exhibit a deeper embedding within the surface.

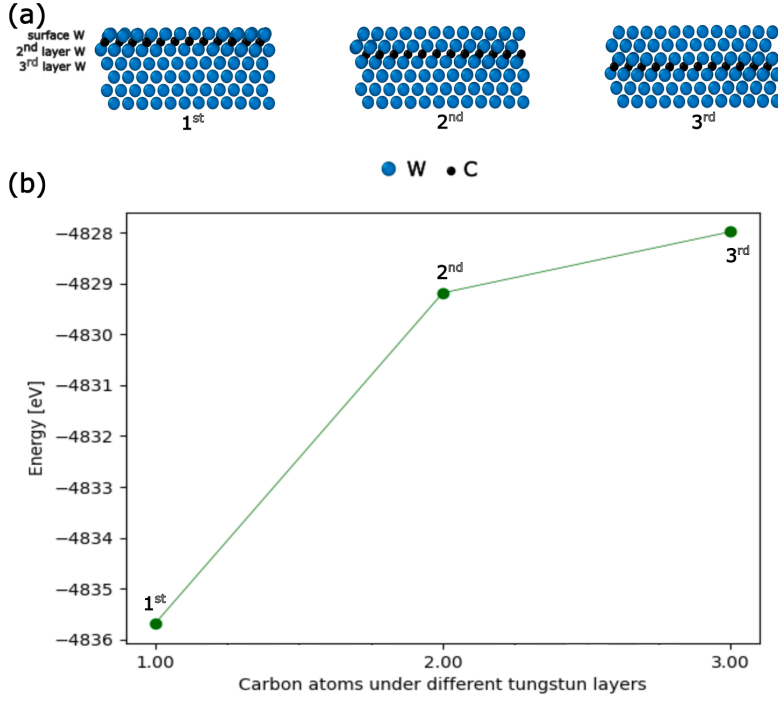


Figure 14: (a) Side view of carburized tungsten systems, where carbon interstitial atoms are deposited under different tungsten layers, from left to right, carbon interstitial layer is under the top surface W layer (1st), under the subsurface W layer (2nd), and under the sub-subsurface W layer (3rd), respectively. Big blue balls indicate W atoms and small black balls indicate carbon atoms. (b) The corresponding total energy of the above-mentioned carburized tungsten systems.

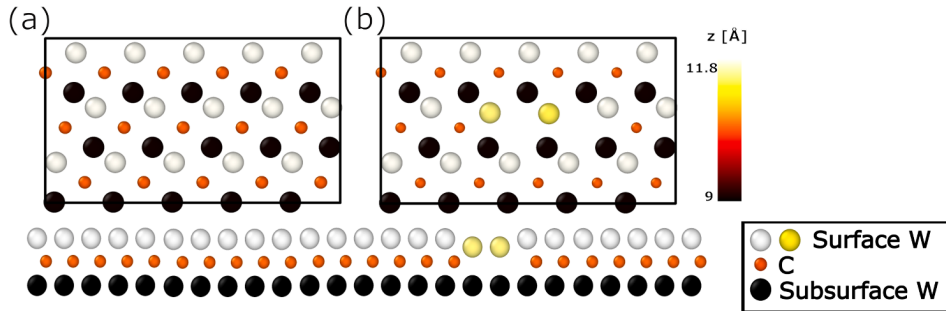


Figure 15: Top and side views of the atomic structure of the smaller R(15x3) unit cell before (a) and after (b) removing 2 carbon atoms. All big spheres represent W atoms in different layers, white balls represent the surface W layer and black balls represent the subsurface W layer, while the small spheres indicate C atoms. Only atoms down to the first W sub-layer are shown. The color coding corresponds to the z-coordinate of the atoms (height).

To gain a deeper insight into the $R(15\times 12)$ surface, I repeatedly observe the atomic-resolution STM image. Previous research [33,36,37,39,40,43,49,75] had observed the B-block shown in Figure 11b, as exhibiting the periodicities characteristic of a clean $W(110)$ surface, they attributed it to a carbon-free region. However, as seen in Figure 11a, the strong features present in the experimental STM image within the B-block are entirely absent in our simulations, but in the top and bottom blocks, where sub-layer carbon interstitials are present, the surface tungsten atoms reside at higher positions, rendering them brighter. This difference led us to question whether the B-blocks are truly clean $W(110)$ areas. Additionally, the carbon-rich A-blocks appear considerably weaker than the B-blocks in Figure 11b, prompting us to propose an opposite stoichiometric relation of the carbon content between the A and B blocks: namely the B-block is carbon-rich, while the A-block is carbon-poor.

Note that the brighter protrusions correspond to surface W atoms with higher z-coordinates. To deduce the atomic positions of interstitial C atoms beneath the top W layer, I hypothesize that the bright protrusions contain a sub-surface layer of C atoms within their $W(110)$ grid cell, while the darker depressions indicate carbon-free regions. Based on this assumption, I analyze Figure 12 by marking the grid cells with solid blue dots to represent those containing a sub-surface C atom, and hollow cyan dots to represent carbon-deficient regions. However, 11 blurred, unmarked cells remain uncertain. To address this ambiguity, all $2^{11} = 2048$ permutations of C atoms being present or absent need to be simulated. To handle this massive set of calculations efficiently, we developed a Machine Learning potential.

To uncover the atomic structure of a WC bi-layer on a pure $W(110)$ substrate, we divided the systems into 11 sets of combinations with equal stoichiometries and examined the energetically favorable configurations where carbon atoms relaxed at various interstitial points, ranging from 36 to 47 C atoms per unit cell. From each set, I selected the structures with the lowest relaxed potential energy values and performed a full DFT electronic relaxation to generate corresponding simulated STM images.

To assess the agreement between the simulated STM images and the observed experimental STM image, I calculated the Pearson correlation coefficient between them. In support of our hypothesis, I obtained several candidate structures exhibiting high similarity to the experimental STM image (Pearson correlation $> 55\%$) in Figure 16 and Figure 17. The structure containing 39 C atoms, which demonstrated the highest correlation, is presented in Figure 16a.

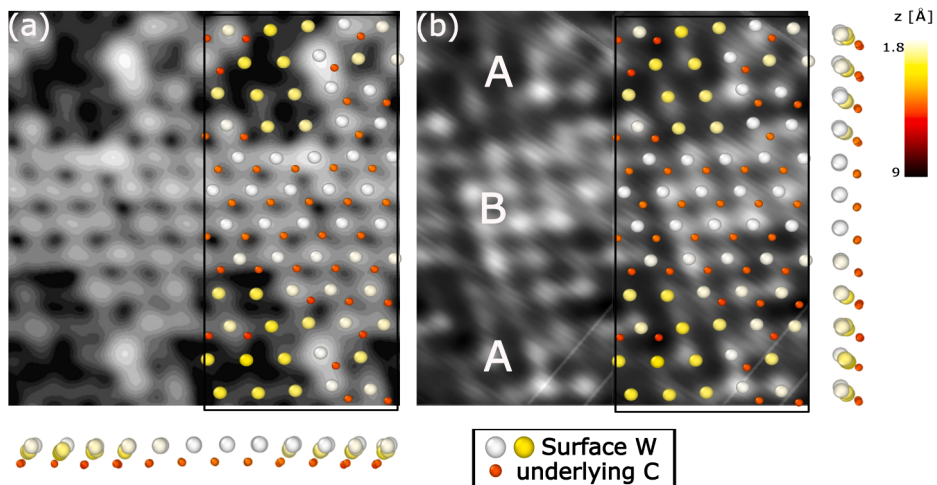


Figure 16: (a) The simulated constant-current STM image of the relaxed structure of the R(15×12) surface at sample bias of + 0.25V. (b) The atomically resolved experimental STM image. The atomic structure of the top W layer and subsurface C atoms is superimposed on both STM images. The color coding corresponds to the z-coordinate of the atoms (height).

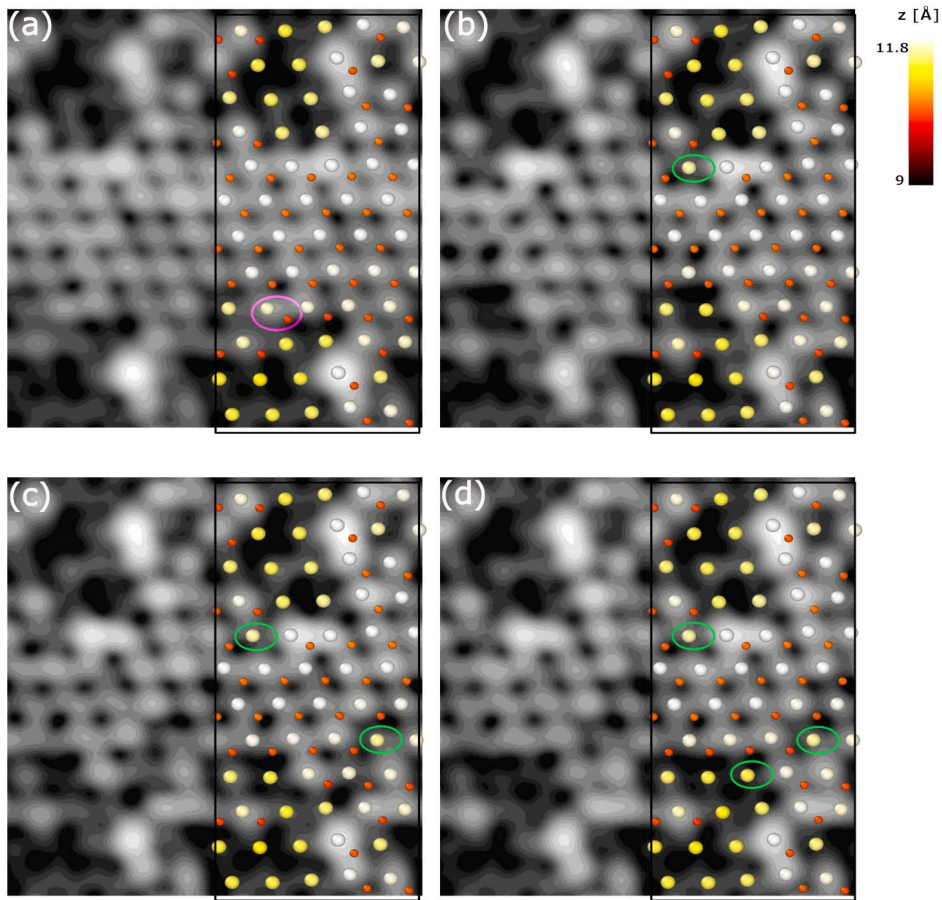


Figure 17: Simulated constant current STM image of the relaxed atomic structure of the R(15 $\times$ 12) reconstruction with different numbers of C atoms. (a) 40 C atoms, (b) 38 C atoms, (c) 37 C atoms, and (d) 36 C atoms. All STM images were simulated for a voltage +0.25V and the corresponding atomic structures are superimposed on them. The top W layer is represented by large spheres, while carbon atoms are smaller ones. Compared to Figure 16b, adding, or removing carbon atoms are indicated by pink or green open circles. The color coding corresponds to the z-coordinate of the atoms (height).

3.3.6 Work function change due to field-induced surface restructuring under fields

After obtaining the best-fit structure for the R(15×12) surface, I further studied its properties when exposed to external electric fields. Bertolini et. al [33] measured a work function change($\Delta\phi \approx -0.4$ eV) using various methods. Since the work function is surface-dependent, applying a high electric field causes restructuring of the R(15×12) surface, resulting in a change in the work function, which can be expressed as:

$$\Delta\phi = -\frac{\Delta\mu}{V} \cdot \frac{1}{\epsilon_0} \quad (19)$$

where $\Delta\mu$ is the permanent dipole moment difference caused by surface restructuring, V is the volume of the unit cell of the R(15×12) surface, ϵ_0 is the vacuum permittivity. Previous research has regarded the R(15×12) surface as a meta-stable structure. We propose that under high electric fields, a portion of surface tungsten atoms may pop out, leading to a negative work function change.

To validate this hypothesis, I performed DFT calculations on the R(15×12) surface in the presence of applied fields. These calculations aimed to observe potential surface restructuring due to the electric field. Unfortunately, based on the current simulations, no surface restructuring was observed.

The absence of observed restructuring in the simulations could be due to several factors, including limitations in simulation time and cell size or the need for even higher electric fields than those tested. Despite this, the theoretical framework and the hypothesis of surface atom displacement under high electric fields remain valid avenues for further investigation. Additional studies, possibly incorporating longer simulation times or more advanced techniques, might be necessary to capture the restructuring phenomena predicted by the theoretical model.

CHAPTER 4

DISCUSSION

In this thesis, a biased self-diffusion on the three lowest-index Cu surfaces ($\{100\}$, $\{110\}$, and $\{111\}$) was observed under an electric field gradient. To validate the MD-FEM electrostatic model, we estimated its polarization characteristics and compared them to corresponding values derived from DFT calculations. The results revealed that the MD-FEM method cannot accurately predict μ_{sr} , as it produced the opposite sign. This discrepancy is likely due to the dependence of adatom dipole moments on surface chemistry, which a purely electrostatic approach struggles to capture. Additionally, the method underestimates α_{sr} by roughly an order of magnitude. This discrepancy can be partially attributed to the different geometries employed in the MD and DFT methods. In MD simulations, a cylindrical atomic system with a needle-like FEM extension was used to maximize the electric field gradient. In contrast, DFT simulations utilized a slab system for computational efficiency, as DFT does not require a gradient. It is expected that the cylindrical MD system would polarize differently from a slab system.

Currently, the proposed MD-FEM model is not adequate to predict quantitatively the biased diffusion characteristics of the adatoms, since the predicted characteristics were found to disagree with the theoretical ones estimated by DFT-calculated polarization characteristics. This limitation originates from the fact that the existing MD-FEM model does not include the important surface polarization effects. This necessitates the development of more advanced methods to incorporate electric fields into MD simulations and subsequently compare the results to direct DFT outcomes. The study of metallic surface behavior under high electric fields heavily relies on accurate polarization characteristics, prompting the question: can the aforementioned simplified equations be trusted? The validity of neglecting hyperpolarizability terms has been tested only for electric fields up to 3 GV/m. To extend this assessment, it is necessary to evaluate the validity for a much wider field range, with Cu nanoparticle structures. The results indicate that disregarding the hyperpolarizability terms is valid for electric fields up to 15 GV/m. This validation supports the calculation approach for surface dynamics based on simplified polarization characteristics equations.

This finding validates the calculation approach for surface dynamics based on Eq. (18) as introduced by Kyritsakis et al. [31]. According to our simulations, Cu nanoparticle structures change dramatically when exposed to applied fields. Despite these substantial modifications, their total energies are still accurately described by the permanent dipole moment μ and polarizability terms α . The total energy curves that neglect hyperpolarizability terms coincide perfectly with those that include these terms, especially for applied fields below 12 GV/m. This consistency indicates that the simplified polarization characteristics are sufficient for

accurately predicting the total energy. The permanent dipole moment μ and the polarizability α presented in

Table 2 show good agreement with each other. Note that μ , α obtained from VASP are based on Eq. (17), i.e., calculated by fitting a straight line on the dipole-field curve obtained from VASP. Meanwhile, μ and α obtained from GAUSSIAN are derived from Eq. (18), i.e., by fitting a parabola to the calculated energy-field curve. The agreement of these parameters confirms that the first two terms are sufficient to predict U and p_z . The results for Cu nanoparticles have confirmed the validity of neglecting the hyperpolarizability terms for field values close to intense FE and VBD.

After confirming the validity of the abovementioned simplified equations for polarization characteristics, the next step is to apply the validated simplified equations to study the work function change of the R(15 $\times$ 12) surface reconstruction under high electric fields. The initial challenge is to elucidate the atomic structure of this specific carburized tungsten system. The results indicate a strong correlation between the predicted atomic positions of the surface W atoms from calculations and the observed bright protrusions in the experimental STM image. Based on the hypothesis, the B-blocks in the simulated STM image are observed as bright protrusions as well. Thus, there are no major brightness differences in different areas between the experimental and simulated STM. This consistency can be ascribed to the presence of a sub-surface carbon layer, which elevates the z-direction coordinates relative to the clean W(110) region. Additionally, the characteristic diamond-shaped structures in the A-blocks are discernible in both the experimental and simulated STM images, further validating the proposed model. Finally, the results align well with the dark regions observed in the experimental STM image, further supporting the proposed atomic structure model. It is clear that these dark depressions are caused by missing underlying C atoms, resulting in virtually clean W(110) areas.

Based on the proposed atomic structure of the R(15 $\times$ 12) surface, an electric field was applied to observe potential structural modifications and resultant work function change, as measured by Bertolini et. al [33]. While Bertolini et al. observed a work function change when the surface was exposed to electric fields, the DFT simulations could not detect the expected structural restructuring. Upon closer analysis, it was found that the key difference between the simulations and the experimental results was the temperature of the system. To tackle this, the next step is to study the R(15 $\times$ 12) surface at 300 K by incorporating external electric fields into MD simulations. This will allow the surface W atoms to potentially overcome the energy barriers, leading to observable structural modifications. The subsequent work function change can then be measured using the polarization characteristics investigated previously.

Finally, this investigation into carburized tungsten covers various aspects, ranging from examining surface reconstructions to understanding the response of these surfaces to applied fields. This work has raised two important questions. The first question concerns the response of the R(15 $\times$ 12) surface to an applied field, which remains unknown and is essential for explaining the work function

change measurement of ref. [33]. The second question is the exact reconstruction mechanism that transforms the W(110)-R(15 $\times$ 3) surface into the W(110)-R(15 $\times$ 12) surface proposed in ref. [75], including the C-removal path and the factors determining the periodicity of each surface reconstruction. Although the available evidence is currently insufficient to answer these questions, our research suggests that the proposed atomic structure is likely the most energetically favorable. This study provides valuable insights into the broader understanding of metal surface dynamics and lays the groundwork for future research.

CHAPTER 5

CONCLUSIONS

This study has explored multiple facets of the behavior of metal surfaces under high electric fields, advancing the understanding of the intricate interplay between surface structure and external electric fields. By addressing key components, such as the MD-FEM model and field-induced surface reconstructions in the presence of applied fields, this work lays a solid foundation for future research in this area.

The biased self-diffusion on Cu surfaces by the presence of electric field gradients, was observed in MD simulations coupled with the finite element solver for calculating electric field distribution at a metal surface. The mechanism of biased diffusion can contribute to the sharpening and regrowth of field-enhancing nanotips, which are proposed to provide particles necessary for plasma formation in vacuum arc breakdowns. However, the diffusion characteristics of the adatoms obtained from the MD simulations do not align well with the predictions of the polarization theory, as calculated via direct DFT calculations. This discrepancy indicates that while the current approach provides qualitative insights into biased diffusion, it is not sufficient for accurate predictions. Thus, there is a need to develop more advanced methods for incorporating electric fields into MD simulations and for comparing these results with direct DFT outcomes.

To verify the validity of the simplified quadratic expansion describing surface energy as a function of the applied electric field, it is necessary to investigate the behavior of Cu nanoparticles with various atomic structures under high electric fields. I compared the field-induced energy as predicted by the polarization characteristics of each structure – μ and α , while disregarding hyper-polarizability terms. The results show that hyperpolarizability terms are negligible in the investigated range below 15GV/m, relevant for electron emission and vacuum breakdown phenomena. Furthermore, the findings demonstrate that reliable values for μ and α can be derived from low-field calculations of the dipole moment, which is accessible in the more computationally efficient and up-scalable plane-wave-basis density functional theory approach. The significant structural modifications observed in the nanoparticles under these high electric fields highlight the importance of accurately incorporating electric fields in atomistic simulations.

Finally, to investigate the work function change of the carburized W(110)-R(15 $\times$ 12) reconstruction under a high electric field, we hypothesize that it is due to field-induced structural atomic modification. A new model for the atomic structure of the R(15 $\times$ 12) surface was proposed, based on the observation that the entire surface of this reconstruction follows the W(110) lattice. Contrary to previous assumptions, the “B-blocks” appearing brighter in the STM image contain a rich sub-surface layer of C atoms, raising the height of the surface W atoms and producing the bright spots seen in experimental STM images. On the other hand, darker “A-blocks” contain a less dense sub-surface layer of C atoms.

Simulations using density functional theory confirmed the stability of the proposed atomic structure, with the relaxed atomic positions and corresponding simulated scanning tunneling microscopy images consistent with experimental observations. When examining the work function change of the R(15×12) surface under high electric fields, it was unable to observe the expected structural restructuring due to the limitations of combining ramp temperature and applied fields in DFT calculations. Despite this, the results form a decisive step towards understanding the surface properties of the carburized W(110)-R(15×12) surface reconstruction, which is necessary for unlocking its full potential for applications such as nanostructure self-assembly and nano-patterning. This work contributes valuable insights into electric field-induced surface restructuring and lays the groundwork for future research aimed at leveraging surface dynamics for technological advancements.

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SUMMARY IN ESTONIAN

Kõrgete elektriväljade mõju metallidele elektronstruktuuride analüüside põhjal

Tugevad elektriväljad mõjutavad metallpindade käitumist märkimisväärselt. Lisaks mehhaanilisele pingele ja elektronide või ionide võimalikule välja-paiskumisele põhjustavad nad ka keerulisi muutuseid aatomite vahelistes interaktsioonides. See võib viia pinna-aatomite difusiooni teatud eelissuuna tekkeni, mis omakorda võib endaga kaasa tuua elektrilise läbilöögi või ka mitmesuguseid muid elektrivälja poolt esile kutsutud pinna muutuseid, näiteks elektrivälja põhjustatud pinna ümber struktureerimist.

Vaakumis toimuva elektrilise läbilöögi fundamentaalsed tekkemehhanismid ei ole veel lõpuni väljaselgitatud. Üks usutavamatest selgitustest on elektrivälja poolt indutseeritud nanoeendite kasv metallipindadel läbi kallutatud difusiooni. Kui pinnale rakenduv elektriväli ületab teatud lävepinge, on võimalik jälgida üksikute metallist teravik-katoodide otstest tulenevaid vaakumläbilööke. Need läbilöögid viitavad pinnal toimuvale protsessile, mis ilmselt viib metallteraviku kasvu ja sellega seoses läbilöögi alguseni.

Atomistliku elektrivälja indutseeritud pinnadifusiooni mudeli valideerimiseks arendati välja molekulaardünaamika lõplike elementide meetodil (MD-FEM) põhinev mudel. Selle mudeli abil sai uurida vase pinnal leiduvate üksikute aatomite (lisa-aatomite) liikumist välise elektrivälja rakendamise puhul. Hinnates efektiivset dipoolmomenti ja polariseeritavust aatomite difusiooniprotsessi põhjal ning võrreldes neid väärtusi tihedusfunktsionaali teooria (DFT) arvutustest saadud väärtustega, leiti, et MD-FEM mudelist tuletatud polarisatsioonikarakteristikud annavad ainult kvalitatiivseid hinnanguid DFT arvutustest saadud täpsete väärtustega võrreldes.

Varasemad uurimused on viidanud, et lisa-aatomite difusioon metallide pindadel omab eelissuunda piki elektrivälja gradienti tugevamate väljapiirkondade suunas. Lisaks võib selliste lisa-aatomite difusiooni kirjeldada aatompolarisatsiooni karakteristikutega, teisisõnu efektiivsete dipoolmomentide ja pinna lisa-aatomite polariseeritavusega. Seda teooriat on hiljuti edasi arendatud ja see näitab, et nende polarisatsiooni karakteristikute korrektseks väljaarvutamiseks ei piisa ainult aatomiga seotud laengutega arvestamisest, vaid tuleb arvesse võtta laengu-tiheduse ümberjaotumist terves aatomi lähipiirkonnas. Kuigi see meetod on olnud nõrkade, kuni paar GV/m, elektriväljade korral polarisatsiooni karakteristikute edukas, ei ole endiselt selge, kas tugevamate elektriväljade korral tohib hüperpolarisatsiooni liikmeid ignoreerida.

Selleks, et arendatud teooriat kontrollida, kasutati vase nanoosakesi tugevas elektriväljas teststruktuuridena. Tulemused viitavad sellele, et selliste osakeste koguenergiat saab uuritud piirkonnas täpselt kirjeldada ilma hüperpolarisatsiooni efektideta.

On oluline silmas pidada seda, et tugevad elektriväljad mõjutavad metallide pindu märkimisväärselt, mõjutades mitte ainult difusiooniprotsesse, vaid ka elektrivälja poolt põhjustatud pinna ümberstruktureerimist. Hiljutises uuringus täheldati umbes 10% muutust emissioonivooludes, kui uuriti R(15×12) karbureeritud volframstruktuuri. Teisest küljest peaks väljastatud vool näitama ligikaudu 1% muutust üheaatomilise pinnasammu (umbes 2 Å) puhul, nagu on eksperimentaalselt täheldatud. Täheldatud 10% muutus, mis on märkimisväärselt suurem oodatud 1% muutusest, viitab võimalusele, et toimub elektrivälja põhjustatud pinna ümberstruktureerimine. Selle ümberstruktureerimise täpne mehhanism on endiselt teadmata.

R(15×12) on karbureeritud W(110) spetsiifiline pinnarekonstruktsioon, mida iseloomustavad nanomeetri suurused perioodilisused selle aatomstruktuuris. Seda on laialdaselt kasutatud šabloonina metallnanostruktuuride, nagu Au, Ag ja Co, kasvu ja iseorganiseerumise protsessides. Hoolimata sellest, et R(15×12) pind on leidnud laialdast kasutust ja tekitanud huvi nii teoreetilistes kui ka eksperimentaalsetes uuringutes, on selle täpne aatomstruktuur siiani teadmata. Selle täpse struktuuri tundmatuse piirab oluliselt selle pinnastruktuuri omaduste mõistmist, sealhulgas ka see, kuidas see struktuur käitub tugevates elektriväljades. See teadmatuse takistab uute funktsionaalsuste uurimist ja potentsiaalsete väljast põhjustatud pinnamuudatuste eksperimentaalset kontrolli. Seetõttu on üha suurem vajadus välja selgitada täpsed aatomstruktuurid ja seletada pinna ümberstruktureerimise aatomtasandi mehhanisme elektriväljade juuresolekul.

R(15×12) pinna aatomstruktuuri jaoks on välja pakutud uus mudel, mis põhineb tähelepanekul, et kogu antud rekonstruktsiooni pind järgib W(110) võret. Tiheduse funktsionaali teooriat kasutavad simulatsioonid kinnitasid pakutud aatomstruktuuri stabiilsust. Stabiliseerunud aatomipositsioonid ja vastavad simuleeritud skaneeriva tunnelmikroskoopia (STM) pildid on kooskõlas eksperimentaalsete vaatlustega. Need tulemused tähistavad otsustavat sammu karbureeritud W(110)-R(15×12) rekonstruktsiooni pinnaomaduste mõistmise suunas. See teadmine on ülioluline pinna täieliku potentsiaali avamiseks rakenduste, nagu näiteks nanostruktuuride iseenesliku moodustumise ja nano-mustrite kujundamise, jaoks.

Kokkuvõttes loob käesolev väitekirj tugeva aluse elektriväljast põhjustatud metallide pinnadifusiooni aatomtasandi simulatsioonimudelite edasiseks arendamiseks. Samuti loob uusi teadmiseid selle mõjust pinna väljasopistuste kasvu, vaakumis toimuva elektrilise läbilöögi tekkepõhjuste ja elektrivälja põhjustatud pinna ümberstruktureerimise kohta.

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PUBLICATIONS

CURRICULUM VITAE

Name: Ye Wang
Date of birth: 26/07/1990
Citizenship: Chinese
E-mail: YeWang_@hotmail.com, yewang@ut.ee

Education:

2019– University of Tartu, Institute of Technology, Ph.D
2013–2016 Beijing Normal University, College of Chemistry, MS.
2009–2013 Lanzhou University, College of Chemistry and Chemical Engineering, BS.

Work experience:

2016.9–2019.8 Chemistry Teacher, Beijing Jingshan School Yuanyang Branch
2015.9–2016.6 Intern Chemistry Teacher, Beijing Jingshan School Yuanyang Branch
2014.9–2015.6 Volunteer teacher, Experimental Primary School of Beijing Normal University
2014.3–2014.9 Teaching Assistant for a material chemistry course, Beijing Normal University

Teaching experience:

2015.9–2019.8 Teaching chemistry
2014.9–2015.6 Teaching conservation of resources and environment
2014.3–2014.9 Teaching material chemistry

Publications:

Wang, Ye; Moradpur-Tari, Ehsan; Zadin, Veronika; Kyritsakis, Andreas. Unraveling the atomic structure of the $R(15\times 12)$ reconstruction of carburized W(110) based on ab initio calculations. *Applied Surface Science*, 643, DOI: 10.1016/j.apsusc.2023.158632
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ELULOOKIRJELDUS

Nimi: Ye Wang
Sünniaeg: 26/07/1990
E-post: YeWang_@hotmail.com, yewang@ut.ee

Haridus:

2019– Tartu Ülikool, tehnoloogiainstituut, doktorant
2013–2016 Beijing Normal University, College of Chemistry, MS.
2009–2013 Lanzhou University, College of Chemistry and Chemical Engineering, BS.

Teenistuskäik:

2016.9–2019.8 Chemistry Teacher, Beijing Jingshan School Yuanyang Branch
2015.9–2016.6 Intern Chemistry Teacher, Beijing Jingshan School Yuanyang Branch
2014.9–2015.6 Volunteer teacher, Experimental Primary School of Beijing Normal University
2014.3–2014.9 Teaching Assistant for a material chemistry course, Beijing Normal University

Õpetamiskogemus:

2015.9–2019.8 Teaching chemistry
2014.9–2015.6 Teaching conservation of resources and environment
2014.3–2014.9 Teaching material chemistry

Publikatsioonid:

Wang, Ye; Moradpur-Tari, Ehsan; Zadin, Veronika; Kyritsakis, Andreas. Unraveling the atomic structure of the R(15×12) reconstruction of carburized W(110) based on ab initio calculations. *Applied Surface Science*, 643, DOI: 10.1016/j.apsusc.2023.158632
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