

First-Principles Study of Thermodynamic and Mechanical Stability of Thin Copper Films Deposited on Tantalum

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The adhesion, stability, and wetting behavior at interfaces between thin Cu films and clean Ta (110) substrates are investigated by *ab initio* calculations using density functional theory (DFT) in the local density approximation (LDA). Interfaces between pseudomorphic body-centered tetragonal thin films of Cu, strained face-centered cubic thin films of Cu, and a single pseudomorphic monolayer of Cu on body-centered cubic Ta (110) surfaces are studied. Various high-symmetry interface configurations are considered for each case. The mechanical stability of the interfaces is studied by the ideal work of separation, while the thermodynamic stability is investigated by the Gibb's excess interface energy. All three interfaces are found to be thermodynamically unstable. An energy-weighting scheme extends the use of the DFT calculations to the case of an incoherent misfitting interface. The incoherent monolayer of Cu on Ta is thereby found to be thermodynamically stable. For coverages by more than a monolayer, the Cu atoms are expected to form 3D islands on top of the Cu monolayer. With respect to interface separation the monolayer is found to be bound more strongly to the Ta substrate than the thin film. Hence failure is expected to occur not at the Cu/Ta interface but inside the Cu.

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I. INTRODUCTION

The increasing use of Cu for metallization pads in integrated circuit devices and the requirement for a reliable diffusion barrier inhibiting Cu from interacting with Si of the semiconductor chip, led to an investigation of Ta as a diffusion barrier and to increased interest in the study of the Cu-Ta interface system¹⁻⁴. An atomic-scale understanding of structure and stability of thin-film heterophase metal interfaces between face-centered cubic (fcc) Cu and body-centered cubic (bcc) Ta are vital for further development and design of such microelectronic devices. Cu and Ta are practically immiscible⁵. Hence thin Cu films grown on Ta substrates represent a good model case for the study of abrupt, nonmatching fcc-bcc heterophase interfaces. The stability, growth mode, wetting, and microstructure of thin Cu films on Ta substrates are therefore of fundamental and technological importance. While fcc/fcc heterophase interfaces have been studied for years (see e.g. Refs. 6,7), the investigation of fcc/bcc interfaces has not been possible in the same way due to a lack of reliable empirical interatomic potentials. First-principles density functional calculations are therefore used in the present investigation to study some simple fcc/bcc interface structures.

The stability, wetting and growth mode of a thin film depend on the balance between the surface and interface energies. The energy balance is given by^{8,9}:

$$\delta = \gamma_f + \gamma_i - \gamma_s \quad (1)$$

where, as indicated schematically in Fig. 1, γ_f and γ_s

are the free surface energies of film and substrate, respectively, and γ_i is the film/substrate interface energy. Thin-film growth by formation of 3-D crystals, known as Volmer-Weber (VW) growth mode, is obtained when $\delta > 0$. Layer-by-layer growth, known as Frank van-der-Merwe (FM) mode, and mixed or Stranski Krastanov (SK) growth mode are obtained when $\delta \leq 0$. This is also the condition for complete wetting and coverage of the substrate by the film. The difference between SK and FM modes is that for the latter the condition $\delta \leq 0$ must hold for each monolayer. In misfitting systems this condition is generally satisfied only for one or a few monolayers, after which the system switches to a SK mode, which is 3D crystals growing on top of one or a few monolayers.

The growth mode is difficult to predict from knowledge of bulk thermodynamic properties. In particular, for the initial stage of thin-film growth the bulk values of surface energies are not necessarily valid because the electronic structure of the thin overlayer can be very different from that of a free surface of a thick film, due to the interaction with the underlying substrate. Furthermore, the energy of an internal solid-solid interface is often not known.

A few deposition experiments of Cu on Ta have been conducted to investigate structure, stability and growth mode of thin Cu films on Ta substrates. Ultrathin Cu films deposited on Ta (110) were studied by Kuhn *et al.*¹⁰. They found that up to coverages of one monolayer or less, Cu forms a stable pseudomorphic film on top of the Ta, i.e., a film which assumes the same structure as the substrate, indicating that the Cu-Ta interaction is stronger than the Cu-Cu interaction. As the coverage increases,

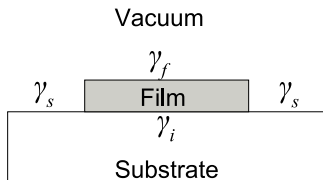


FIG. 1: Schematic drawing indicating the interface and surface energies in the thin film growth mode criterion of Eq. (1).

up to 1.22 ML, the morphology of the film changes to a more densely packed 2D film with a mismatch occurring along the $[1\bar{1}0]$ direction of the substrate. Additionally deposited Cu atoms form 3D clusters above the 2D films. Kuhn *et al.* conclude that a 1.22 ML coverage presents an equilibrium between two opposing forces on Cu, namely the strain inside Cu due to the coherency, and the interfacial Cu-Ta interaction which drives the coherence between Cu and Ta. Similar results for the monolayer stability and morphology were obtained by Chen *et al.*¹¹ for Cu deposited on a clean, oxide free polycrystalline Ta substrate. At sub-monolayer (2 Å) coverage of Cu a pseudomorphic monolayer was stable both at room temperature and after annealing at a temperature of 1000K. However, for Cu coverage of 5 Å and more, dewetting of Cu from Ta was observed¹¹.

More recently, Venugopal¹² found that Cu films, which are deposited on Ta(110) and Ta(100) at room temperature up to a thickness of 50 Å, are metastable. Upon heating, the films breakup and agglomerate into islands leaving one or two monolayer thick Cu films on the Ta substrate. It was also shown that μm -sized Cu islands had a fcc crystal structure with (111) planes parallel to the substrate surface and with the Nishiyama-Wasserman orientation relationship (NW): $(111)_{\text{fcc}} \parallel (110)_{\text{bcc}}$ and $[1\bar{1}0]_{\text{fcc}} \parallel [1\bar{1}1]_{\text{bcc}}$. On the other hand, Kim *et al.*¹³ reported that 20 nm thick Cu films deposited on Ta substrates and annealed under UHV conditions agglomerate into small islands¹³ with a non-wetting contact angle of $123 \pm 8.5^\circ$ and no evidence for monolayer coverage.

Molecular dynamics simulations of Cu deposition on Ta by Klaver and Thijsse^{14,15} indicated that Cu atoms deposited on Ta (110) and (100) substrates form stable mono-crystalline films with a "fish-bone" or "rippled" structure, on top of which 3-D island growth of Cu was observed. Upon further deposition, the Cu islands coalesce and form an almost perfect fcc bulk structure.

The available experimental values for the free surface energies of Cu and Ta, as well as values obtained from various first-principles and empirical-potential based atomistic calculations^{16–21} can be summarized as follows: The surface energy of Ta is rather large, with an experimental value of 2.5 J/m^2 ¹⁶, and theoretical values of $2.4\text{--}3.0 \text{ J/m}^2$ ²⁰. The experimental value of the surface energy of Cu (111) is 1.8 J/m^2 ¹⁶, and the theoretical values

are $1.4\text{--}2.07 \text{ J/m}^2$ ^{17,18}. The balance of the experimental surface energies according to Eq. (1), indicates that Cu should completely wet the Ta surface provided that the interface energy γ_i is not larger than 0.7 J/m^2 (cf., e.g., Ref. 22). The reported stability of a monolayer of Cu therefore correlates well with the reported surface energies. However, the observed dewetting of the Cu from Ta, as demonstrated convincingly in Refs. 11 and 13 is rather unexpected. One possible explanation of this discrepancy could be that the presence of a monolayer of Cu is not detected when large 3D clusters of Cu are on top, and that this was interpreted as dewetting. Since Refs. 10 and 11 suggest that a pseudomorphic monolayer of Cu on Ta (110) is stable, and that the morphology of this layer depends on the coverage, it may be concluded that Cu grows on Ta(110) first in a layer-by-layer mode and then switches to a 3D growth mode after a number of monolayers of Cu. The relation between the number of stable Cu monolayers and the instability point is unclear. A better understanding of the energy balance as expressed in Eq. (1), in particular pertaining to the interface energies, would lead to a better insight into the specific processes which lead to the instability of the Cu thin films and the wetting behavior of Cu on Ta.

In the current study, first-principles density-functional theory (DFT) calculations in the local density approximation (LDA) are employed to study the adhesion and growth of a thin epitaxial Cu film on bcc Ta (110) surfaces. Two distinct cases are considered, a thin film composed of one monolayer (ML) of Cu on Ta (110), and a thin film composed of up to eight Cu layers stacked in either fcc or bcc structures above the Ta (110) substrate. The stability of a thin Cu film on Ta (110) is investigated both from a mechanical and a thermodynamic points of view via the work of separation and the excess interface energy, respectively. The first-principles DFT method provides a means to calculate independently the various quantities in Eq. (1) and hence allows the determination of the growth mode and wetting behavior of Cu on Ta. It therefore complements the previous experimental and atomistic studies. The immiscibility of Cu and Ta suggests that abrupt interfaces form between Cu and Ta. This makes the Cu/Ta system particularly attractive for DFT calculations as simple abrupt models for the interface can be used.

II. THE CALCULATION METHOD

The computational first-principles method used in the present study is based on density functional theory^{23,24} and the local-density approximation for exchange and correlation (LDA)^{25,26} employing norm conserving pseudopotentials²⁷ and a mixed basis of localized orbitals and plane waves^{28–33}. Previous DFT studies have shown that calculations with the LDA produced reliable results for both Cu and Ta^{34–36}. The pseudopotentials were constructed from all-electron va-

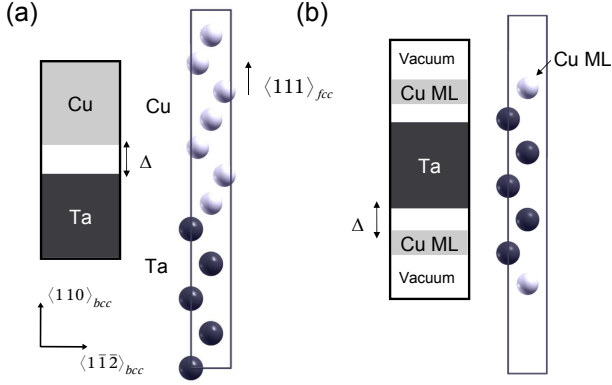


FIG. 2: A schematic sketch of the supercell models for the film in (a) and a monolayer in (b), respectively. The supercell is shown here from a $[1\bar{1}1]$ direction (pointing out of the page).

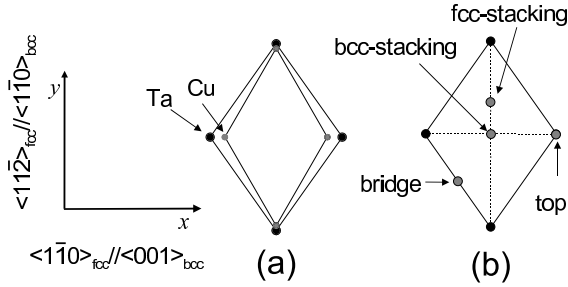


FIG. 3: Schematic view of the Ta bcc (110) (black) and Cu fcc(111) (gray) surface unit cells. The calculated bulk lattice parameters are 3.25 Å, and 3.56 Å for Ta and Cu, respectively. In (a) the incommensurate cells are shown on top of each other. In (b) the commensurate cells (strained Cu on unstrained Ta) are shown together with the different locations considered in this study for the Cu monolayers with respect to Ta substrate.

lence states for free atoms according to the procedure by Vanderbilt³⁷. The following electronic configurations were used: Cu ($3d^{9.40}, 4s^{0.80}, 4p^{0.80}$), and Ta ($4f^{14}, 5d^{3.6}, 6s^{0.6}, 6p^{0.8}$). Plane waves up to the cut-off energy $E_{pw} = 16$ Rydberg were used (1 Rydberg = 13.606 eV). Localized functions confined to the centered spheres with radii $R_{10}^{Ta} = 2.5$ Bohr, and $R_{10}^{Cu} = 2.0$ Bohr (1 Bohr = 0.529 Å) were employed for d valence states. A Monkhorst-Pack $8 \times 8 \times 2$ k-point mesh and a Gaussian broadening by 0.05 eV were used^{29,38}. These parameters led to convergence of differences in surface energies to less than 0.05 J/m².

A. Supercell models

The interface system of the thin Cu film on the Ta substrate is modeled by a slab configuration, where the Ta substrate is composed of five atomic (110) layers, and the thin Cu film is composed of either seven or eight atomic layers. For the pseudomorphic monolayer case, the Cu atoms in the monolayer arrange in the same structure as in the underlying substrate. Each atomic layer is represented by one atom per surface unit cell as shown in Fig. 2, and periodic boundary conditions parallel to the surface. Periodic boundary conditions are also used in the perpendicular direction, hence the supercell shown in Fig. 2(a) for the thin film contains two equal Cu-Ta interfaces. For the ML system, one Cu layer is positioned on each side of the Ta (110) slab as shown in Fig. 2(b), with a sufficiently thick vacuum region to ensure negligible interaction between the two free surfaces.

Figure 3(a) displays a top view of the interface unit cells of Cu (111) and Ta(110) containing only one plane of Cu and Ta, superimposed and aligned according to the NW orientation relationship. A pseudomorphic first layer of Cu is obtained by straining the Cu (111) surface unit cell to match exactly the Ta (110) surface unit cell. In this case a number of high-symmetry positions for Cu atoms are possible as indicated in Fig. 3(b). The translations considered here are: 1) top positions, where a Cu atom is situated above a Ta atom. This is expected to be the least stable configuration but is considered for completeness. 2) Cu on a bridge position at half the Ta-Ta bonds. 3) fcc-stacking sites, where the Cu atom is positioned at one-third of the distance along the long diagonal of the unit cell, and 4) Cu on hollow positions, which is equal to bcc-stacking sites.

For the case of a thin film, further atomic layers of Cu are added to give either a fcc or a bcc Cu lattice. For a fcc lattice, only the first Cu monolayer is really pseudomorphic to the Ta bcc lattice, the other Cu layers are strained fcc to accommodate the mismatch, which results in a coherent 1×1 interface. A pseudomorphic thin film of Cu results for bcc lattice. In this case only the on hollow translation is considered, i.e., the Cu lattice is in perfect registry with the Ta lattice. The axial elastic response of the Cu film to the lateral strain is included for both the pseudomorphic and coherent fcc lattices. Corresponding to the various interface translation states, the Cu film is composed of seven layers for the top, bridge, hollow, and pseudomorphic systems, and eight layers for the fcc-stacking system.

B. The Work of Separation

The ideal work of separation, W_{sep} , of an interface is calculated as the difference in total energy of the system where the two parts are infinitely separated from each other (i.e., a system of free surfaces) and of the system where the two parts are at a finite interaction distance

Δ . Both quantities are of course normalized by the total interface area. W_{sep} is obtained by rigidly separating the thin film (or monolayer) from the substrate without allowing for further relaxation of the cleaved sublattices. W_{sep} calculated in this manner gives direct information regarding the strength and bonding of the interface (for a comparison of rigid and relaxed work of separation cf., e.g., Ref. 21). The rigid W_{sep} is optimized with respect to the interfacial separation by calculating W_{sep} as a function of the interface separation Δ , and fitting for instance the universal binding energy relation³⁹ to the calculated W_{sep} data points. It has been shown²¹ that the rigid W_{sep} is an excellent measure for the mechanical stability and chemical bonding at the interface, provided of course that full atomic relaxations do not result in substantial changes to the energies of the interface and free surfaces. In the current study, a relaxed W_{sep} calculation is performed for the most stable interface so that the effect of relaxation can be estimated. The work of separation is positive for stable interfaces.

C. The Interface Excess Energy

To obtain a thermodynamic assessment of the stability of the monolayer the excess interface energy is needed. The excess interface energy is defined as the total energy difference per interface area between a configuration that includes an interface, and one in which the same number of atoms are in their respective bulk environments. The thermodynamic quantities which need to be determined are Gibb's free energy of the interface, and the chemical potentials of fcc Cu and bcc Ta. In the current study both are approximated by the total energies at zero temperature, which are readily obtained from the ab-initio calculations. Hence, under these assumptions, and in the case of a periodic slab geometry the excess interface energy can be expressed as:

$$\gamma = (E - \sum_i n_i \mu_i) / 2A \quad (2)$$

where E is the total energy of the system, n_i and μ_i are the number of atoms and chemical potential of species i . Since for the interface models the Cu is strained in order to make the fcc (111) planes of Cu commensurate with the (110) planes of Ta, this form of γ includes explicitly the strain energy contribution which scales with the number of atomic layers of Cu. An alternative approach is to substitute for μ the energy μ' of a Cu atom in a bulk configuration strained in exactly the same manner as in the interface model. In what follows, quantities with respect to strained bulk Cu are denoted with a prime. As a consequence the same strain energy is contained in the two terms in the nominator of Eq. (2) and will therefore cancel. The resulting strain-free excess energy, γ' , only includes the energies resulting from purely chemical contributions. (For the definition of chemical contribution and strain contribution to the excess interfacial energy see Ref. 40). Such a procedure is equivalent to the one

used for the calculation of the rigid work of separation above, and is suitable for the study of the mechanical stability and chemical bonding at the interface. It is *not* suitable to assess the thermodynamic stability of the system.

We note that, in the case of a free monolayer of Cu on top of Ta, the resulting excess energy from Eq. (2) calculated with the supercell configuration in Fig. 2(b) contains the excess energies due to the free surface of the monolayer to vacuum *and* due to the interface between the monolayer and substrate, $\gamma_{ML} = \gamma_f + \gamma_i$.

III. RESULTS AND DISCUSSION

A. Bulk and surface energies

The cubic lattice parameters of bulk fcc Cu and bcc Ta crystals obtained in the current study from calculated energy-volume curves are $a_{Cu} = 3.56 \text{ \AA}$ ($a_{Cu}^{exp} = 3.615 \text{ \AA}$ ⁴¹), and $a_{Ta} = 3.25 \text{ \AA}$ ($a_{Ta}^{exp} = 3.3058 \text{ \AA}$ ⁴¹). As shown schematically in Fig. 3(a), this results in a lateral misfit between the Cu (111) and Ta (110) planes. Calculated relative to the equilibrium lattice constant of Cu, the misfit strain is: $\mathbf{e}^{\parallel} \simeq (0.29, 0.05)$ in the $[1\bar{1}0]$ and $[11\bar{2}]$ directions of the fcc lattice, respectively. For the interface models, the Cu is strained laterally by $\mathbf{e}^{\parallel}$, and as a result it will contract normally to the interface. The amount of normal strain was calculated separately by varying the normal strain for a fixed $\mathbf{e}^{\parallel}$ for both the commensurate fcc and pseudomorphic bcc lattices. This resulted in a reduced Cu interplanar separation in the (111) direction of the commensurate fcc lattice by almost 10%: $d_{111} = 0.9d_{111}^0$, while for pseudomorphic bcc Cu, $d_{110} = 0.86d_{111}^0$. From our first-principles calculations, the free surface energy of a relaxed Ta (110) surface is $\gamma_{Ta} = 2.6 \text{ J/m}^2$, compared to the experimental value of 2.5 J/m^2 ¹⁶, and other theoretical values of 2.4 - 3.0 J/m^2 ²⁰. The surface energy of a relaxed Cu (111) surface is calculated to be $\gamma_{Cu} = 1.54 \text{ J/m}^2$, compared to the experimental value of 1.8 J/m^2 ¹⁶, and other theoretical values of 1.4 - 2.07 J/m^2 ^{17,18}. For a fcc Cu film at the commensurate interface, which is under lateral tensile and axial compressive strains the surface energy relative to an equally strained bulk is $\gamma'_{Cu} = 1.44 \text{ J/m}^2$.

B. Mechanical Stability

The ideal work of separation for the strained Cu film W_{sep}^i , and for the ML of Cu W_{sep}^{ML} , on Ta (110) substrate in the various configurations are summarized in Table I. The fit of the universal binding energy curve³⁹ to the calculated interface binding energy data points is shown in Figs. 4(a) and (b) for the film and ML, respectively. In the case of the coherent fcc film, the largest work of separation is obtained for the interface model having Cu atoms on hollow sites which corresponds to a bcc-stacking

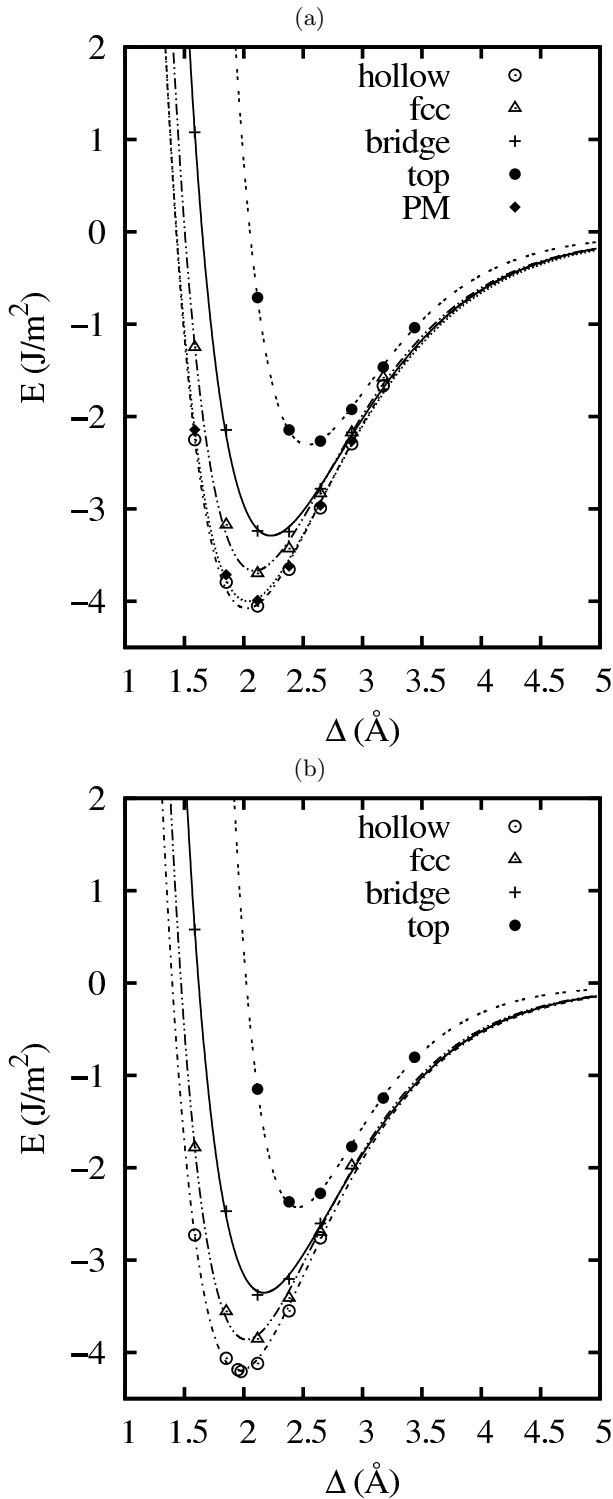


FIG. 4: The interfacial binding energy (the negative of W_{sep}) for (a) a thin Cu film and (b) a Cu monolayer on a Ta substrate, shown as a function of interfacial distances for the various translations considered in the current study. Notice the similarity of the work of separation curves for the pseudomorphic (PM) and hollow cases.

of the first Cu monolayer above the Ta (110) surface. In all cases the difference in W_{sep} between a monolayer and a thin film are small, but the monolayer has consistently higher work of separation than the film. Consequently the monolayer is more strongly bound to the substrate than the thicker film, which is in accordance to studies of bonding at free metal surfaces (cf., e.g., Ref. 42). The work of separation for the pseudomorphic bcc film of Cu (see Table I and Fig. 4) is practically indistinguishable from that of the on-hollow fcc film. For all interfaces considered, the most stable interface configurations are obtained when the Cu atom in the first layer are on hollow positions. The on-top sites of the fcc film, on the other hand, have more than 1 J/m^2 lower W_{sep} than the other translations.

The fact that the work of separation is similar for the three low-energy systems is a consequence of the calculation scheme of the rigid work of separation, where the separated free interfaces are not allowed to relax. Hence bulk properties of the separated Ta and Cu slabs are effectively canceled out, so that the result is dependent purely on interfacial properties.

The failure of the Cu/Ta interface system subject to a tensile stress may either happen in the Cu side, in the Ta side, or directly at the interface between Cu and Ta, depending on the value of W_{sep} for each of the cases. The resulting work of separation for cleaving inside the Cu above the first monolayer is found to be independent of the translation state and equal to $W_{sep}^{Cu} = 2.9 \text{ J/m}^2$. Hence $W_{sep}^{Cu} < W_{sep}^i$ for all translations (except for the unstable on-top case). W_{sep} for cleaving inside Ta, leaving one monolayer of Ta adjacent to the film turns out to be much more expensive than cleaving at the interface or in Cu: $W_{sep}^{Ta} = 6.2 \text{ J/m}^2$. Hence the Cu/Ta interface system is more prone to mechanical failure in Cu away from the interface. This should have profound implications for growth processes as well as for the formation of pores, the propagation of cracks and the interaction of dislocations with the interface.

System	Thin Film		Monolayer	
	Δ^i	W_{sep}^i	Δ^{ML}	W_{sep}^{ML}
top	2.55	2.31	2.46	2.43
bridge	2.23	3.29	2.17	3.36
fcc-site	2.09	3.68	2.03	3.86
hollow	2.08	4.08	1.99	4.24
PM	2.04	4.00		

TABLE I: The equilibrium interfacial separations Δ^i and Δ^{ML} (in $\text{\AA}$) and the work of separation W_{sep}^i and W_{sep}^{ML} (in J/m^2) for the thin-film interface (i) and monolayer (ML) systems, respectively. PM refers to the pseudomorphic interface.

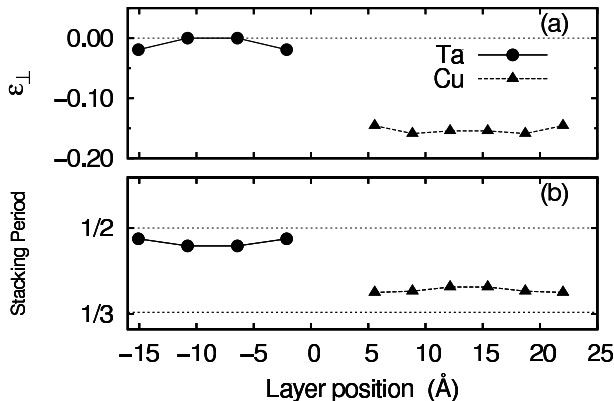


FIG. 5: In (a) the axial strain, $\epsilon_{\perp}$, normal to the interface in Cu and Ta is plotted as a function of the layer position. In (b) the stacking period along the $[1\bar{1}0]_{bcc}$ and $[11\bar{2}]_{fcc}$ directions of bcc Ta and fcc Cu, respectively, are shown. The dashed lines in the lower panel at 1/3 and 1/2 indicate the ideal stacking periods of Cu (111) and Ta (110) planes, respectively.

C. Full atomic relaxation

The work of separation for the fcc film with Cu on hollow sites was calculated including the full relaxation of all atomic positions at the interface and at the separated surfaces. This relaxation was performed for a number of starting configurations with different interface separations. The total energy and forces of all systems are compared, and the one with the minimum energy for zero forces is the final relaxed system. Hence the relaxation takes into account also the optimization of the normal supercell dimensions in addition to the relaxation of the atomic positions, but not the lateral lattice parameters, which are kept fixed.

The relaxation resulted in an increase in the compressive axial strain in Cu by nearly 5% (from an initial 10% to a final 15%) as shown in Fig. 5(a). A compressive strain is also evident at the interface layers of Ta, but no change in the axial strain occurred in the bulk layers. Hence only the Ta surface is affected by the relaxation, while for Cu the strain is distributed uniformly across the thin film.

In the lateral direction, the interplanar separation in Cu is increased, while that in Ta is decreased. This is evident in Fig. 5(b) from the stacking period of Cu and Ta calculated along the $[11\bar{2}]_{fcc}$ and $[1\bar{1}0]_{bcc}$ directions, respectively. The stacking period is defined as the translation distance of two consecutive Cu (111) and Ta (110) planes projected onto the surface unit cell, and given in units of the unit cell length. The ideal stacking period of Cu (111) planes along the $[11\bar{2}]_{fcc}$ direction is $\frac{1}{3}$, which corresponds to the “ABC” stacking of the (111) planes, and the ideal stacking period of Ta (110) planes along the $[1\bar{1}0]_{bcc}$ direction is $\frac{1}{2}$, which corresponds to the “AB” stacking of (110) planes. The change in the stacking pe-

riod resulted in an alignment of Cu and Ta planes along the $[1\bar{1}1]$ direction of the bcc Ta lattice. Hence there is a general tendency to produce a matching interface between the fcc Cu and bcc Ta.

The resulting work of separation of the relaxed system is $W_{sep}^{relax} = 3.73 \text{ J/m}^2$, which is 0.35 J/m^2 less than the corresponding rigid work of separation. The resulting relaxed Cu-Ta interfacial separation is $\Delta = 2.06 \text{ \AA}$, which is very close to the values obtained from the rigid work of separation calculation for both the hollow and pseudomorphic systems given in Table I. Hence, the full atomic relaxation did not result in a large change in the ideal rigid work of separation. It is expected that the work of separation of the other translation states change in the same manner. This demonstrates that the rigid W_{sep} may be used effectively to estimate the mechanical stability of the interfaces²¹.

D. Thermodynamic Stability of the Monolayer and a Thin-Film

The results for the rigid W_{sep} given so far indeed demonstrate that a ML is mechanically more stable on a Ta (110) surface than a thin film. However, this does not necessarily mean that a ML is also thermodynamically more stable than a film or a free substrate surface. For this we need to consider the interface excess energy calculated using Eq. (2) for the thin film, γ_i and monolayer, γ_{ML} , which are summarized in Table II. The related strain-free excess energy calculated with respect to a strained bulk Cu, γ'_i and γ'_{ML} , for the film and ML, respectively, are also given in Table II.

The excess energy of the thin film system γ_i scales with the volume of Cu due to the misfit strain. Due to this dependency on volume, this quantity is not very meaningful for the stability of the interface from thermodynamic considerations. However, for completeness it is also given in Table II. The difference in energy between the system with Cu on fcc stacking site, where eight Cu layers are in the system, compared to seven layers in the other translation states of course is due to this volume term.

We also note again that the calculated excess energy of the thin film contains the contribution arising from the internal Cu-Ta interfaces, whereas that of the ML contains both the internal interface energy and the energy due to the free ML surface.

It is obvious from the results in Table II that the excess energy γ_{ML} of the ML exceeds the value of free Ta (110) surface energy, $\gamma_{Ta} = 2.6 \text{ J/m}^2$, resulting in $\delta > 0$ in Eq. (1) for all translation states. We conclude therefore that simple models of either a coherent fcc or a pseudomorphic bcc monolayer of Cu on Ta (110) result in unstable interfaces, and thus will not likely describe the structure of realistic thin Cu films on Ta.

However, while our calculations indicate that a pseudomorphic ML is unstable, a more general interface struc-

System	Thin Film		Monolayer	
	γ_i	γ'_i	γ_{ML}	γ'_{ML}
top	8.8	1.90	5.31	3.33
bridge	7.9	0.91	4.39	2.40
fcc-site	8.4	0.45	3.88	1.90
hollow	7.05	0.12	3.51	1.52
PM	6.79	0.21		

TABLE II: The excess interface energies (in J/m²) at equilibrium separations for the interface, γ_i , and for the monolayer, γ_{ML} , of Cu on Ta (110) surface. Primed quantities refer to excess energies calculated with respect to strained bulk Cu. PM refers to the pseudomorphic interface.

ture should be considered since in lattice mismatched systems one expects the formation of a semi-coherent interface consisting of nearly perfectly matched coherent regions separated by interface dislocations which arise in order to relieve the lattice mismatch across the interface. The direct calculations of the excess energy of such realistic interface models from first-principle methods is not yet feasible because it would require too large systems. Nevertheless, in the following we describe a method to estimate reasonably the excess energy of an incoherent ideal interface based on rather basic assumptions similar to those utilized recently by Benedek *et al.*⁴³.

We consider a general commensurate interface formed by putting two ideal Cu and Ta crystals together in the NW orientation relationship without straining any of the lattices. A commensurate interface is characterized by a 2D repeat cell of finite area in the interface plane²². For the coherent models considered so far, the Cu is strained such that the 2D repeat area is equal to the Ta (110) surface unit cell. For a general interface, a 2D repeat cell is obtained by repeating the surface unit cells of unstrained Cu and Ta $m \times n$ times along the x and y directions shown in Fig. 3, such that the resulting residual geometrical misfit is negligible. In the current case, 22×19 times the Cu spacing along the $[1\bar{1}0]_{fcc}$ and $[11\bar{2}]_{fcc}$ directions fit with 17×18 times the Ta spacing along the $[001]_{bcc}$ and the $[1\bar{1}0]_{bcc}$ directions. This results in a residual misfit strain of less than 10^{-3} in both lattices.

The interface 2D repeat cell thus formed is shown in Fig. 6, where only one plane of Cu and Ta at the interface are shown. The Cu atoms are represented by the small spheres, and the Ta by the large dark spheres. The color shading of the Cu spheres corresponds to local energies as described in what follows. The Cu atoms at the interface plane of the incoherent and unrelaxed interface experience a variety of coordinations with respect to the underlying Ta atoms. Some Cu atoms are situated on hollow sites, some on bridge sites, some on fcc-stacking sites, and some on top sites, while others are off center from these high-symmetry locations. Such atoms may be assigned to the symmetry types they resemble most

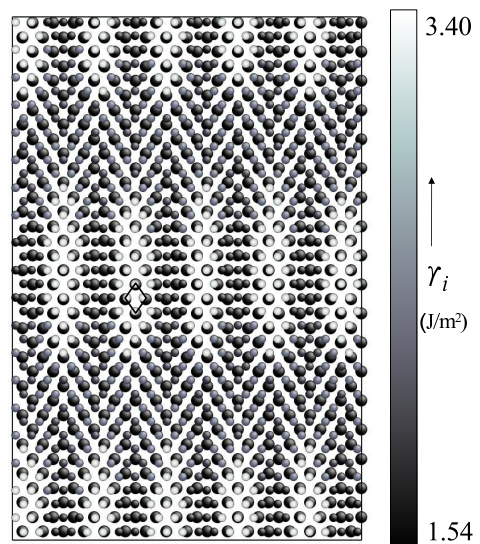


FIG. 6: A cross section of the 2D repeat cell for a general incoherent but commensurate Cu-Ta interface in the NW orientation relationship. Only one Cu and Ta layer is shown at the interface. Ta atoms in the bcc (110) plane are shown as large dark spheres, while Cu atoms in the fcc (111) plane are shown by small spheres represented with different shades of gray corresponding to the local effective excess energy for $n = 1$, cf. Eq. (3). Dark small spheres represent Cu atoms with low local energy, while bright small spheres represent Cu atoms with high local energy.

closely. We define a local contribution to the total interface excess energy arising from each particular site, where the energy of the local site is derived from the energy of the nearest symmetry sites of the corresponding coherent interface model. Since we assume an incoherent interface with negligible misfit strain, the strain-free local excess energy of the coherent system must be used (i.e., the primed quantity γ'). We define a local excess energy contribution from each atomic site i at position r_i , $\gamma'(r_i)$ as a weighted sum of the excess energies of all nearest high-symmetry sites, with a weight exponentially decaying with distance from the site, namely:

$$\gamma'(r_i) = \sum_{s=1}^n \gamma'_s e^{-r_{si}} / \sum_{s=1}^n e^{-r_{si}} \quad (3)$$

where r_{si} is the distance between the Cu atom at position r_i and the symmetry site s , γ'_s is the strain-free coherent interface energy for the symmetry type of site s , which corresponds to either on hollow, on bridge, fcc-stacking, or on top sites, as given in Table II. The sum over s spans the first n nearest symmetry sites to the Cu atom site at position r_i .

The excess energy of the whole interface is obtained by

n	$\tilde{\gamma}_{ML}$	$\tilde{\gamma}_i$	$\tilde{W}_{sep}^{ML}$	$\tilde{W}_{sep}^i$
1	2.41	0.96	3.35	3.23
2	2.34	0.88	3.42	3.3
3	2.30	0.84	3.47	3.34
4	2.30	0.84	3.46	3.33

TABLE III: Effective total excess energy and work of separation (both in J/m²) for $n = 1$ to 4 in Eq. (3) for a ML and a thin film.

summing the local contributions across the interface:

$$\tilde{\gamma}_{ML} = \frac{1}{N} \sum_{i=1}^N \gamma'(r_i) \quad (4)$$

where N is the total number of Cu atoms in the interface layer. For the case $n = 1$, this would be equivalent to the simplest scheme where each atomic site is assigned to the nearest symmetry site. The result for $n = 1$ is presented graphically in Fig. 6 by the different gray-scale shading of the Cu atoms. Dark small spheres represent Cu atoms positioned on hollow sites which have the lowest excess energy, while the bright small spheres represent atoms positioned on top sites which have the highest excess energy. Atoms represented by various shades of gray correspond to off-symmetry sites. The whole Cu and Ta layers were also translated rigidly with respect to each other to minimize the excess energy. However the possible energy gain was found to be quite small. It is only of the order of 0.1 J/m². The total effective excess energy estimated from Eq. (4) for a varying number of nearest symmetry sites is given in Table III. The effective excess energy is reduced as n increases up to $n = 3$ where it stabilizes. The important point is, however, that the effective excess energy $\tilde{\gamma}_{ML}$ is lower than that of the free surface energy of the (110) surface of the Ta substrate for all cases. Since the effective excess energy $\tilde{\gamma}_{ML}$ of the incoherent commensurate interface is an upper estimate for the relaxed excess energy of a realistic semi-coherent interface between the Cu ML and the Ta (110) substrate, we conclude that without requiring a pseudomorphic interface, and without imposing strain in the ML, the ML is thermodynamically stable.

We extend this scheme now to the rigid work of separation of the ML and the thin film, as well as for the excess energy of the thin film. The results are presented in Table III. Note that for a thin film, the effective incoherent interface energy $\tilde{\gamma}_i$ calculated in this scheme does not take into account the substantial effect of inhomogeneous strain in the bulk of the film, and hence it does not necessarily reflect the film's stability.

Whether a second Cu ML on Ta surface is stable or not, cannot be derived from the above energy-weighting scheme. Further experiments, or computational simulation approaches, which enable the study of atomistic large-scale structures, such as molecular dynamics with

carefully designed interatomic potentials would serve better to address this issue.

From the data in Table III the work of separation for cleaving in the Cu film leaving an incoherent Cu ML on the Ta can be estimated. The work of separation for cleaving in Cu between the Cu ML and the rest of the Cu film is:

$$\tilde{W}_{sep}^{Cu} = \gamma_{Cu} + \tilde{\gamma}_{ML} - \tilde{\gamma}_i \quad (5)$$

which results in $\tilde{W}_{sep}^{Cu} = 2.88$ J/m² or 3.0 J/m², calculated with $n = 1$ or $n = 4$, respectively, from data in Table III. This result is very similar to that found for the rigid relaxation above, and it is still smaller than $\tilde{W}_{sep}^i$. Hence also for the case of a general interface, a tensile test on the Cu/Ta interface should lead to a failure within the Cu film.

It may be argued that the lateral dilation present in the Cu in all the coherent interface models used in the present study, may further lead to an enhanced interaction between the Cu and Ta layers at the interface, similar to that leading to the out-of plan contraction. As a result, the work of separation W would be overestimated, while the excess interface energy γ would be underestimated. However, as we show in the following this effect is negligible. If we assume a substantial enhancement of the Cu-Ta interaction across the interface, it would lead to a very small Cu-Ta interface separation relative to the interplanar separations in bulk Cu and Ta. However, by comparing the interface separations obtained from the fully relaxed system (see section III C) $\Delta = 2.06$ Å, and from the rigid work of separation calculation results listed in Table I, it is evident that the interface separation is very close to the mean bulk interplanar separations in (unstrained) Cu and Ta: $d = 2.17$ Å, indicating that the interaction across the interface is not substantially affected. Furthermore, a quantitative estimate of the strain effect may be obtained from the excess energies of *free* slabs of strained and unstrained Cu. Indeed, as already given above (section III A), the surface energy of a free strained Cu slab is underestimated, however the difference is small, $\gamma_{Cu} - \gamma'_{Cu} = 0.1$ J/m². Note that γ'_{Cu} is measured as the true excess energy with respect to equally strained bulk Cu. This effect is expected to be much smaller for the case of the Cu-Ta interface, since for an interface with vacuum the interactions within the surface layer are expected to be more enhanced than those for the case of an interface with a second metal.

However, even by taking this value of 0.1 J/m² into account in the calculation of $\tilde{\gamma}_{ML}$ in Eqs. 3 and 4, the resulting effective excess energy of the incoherent interface would still be smaller than the free surface of Ta, albeit by a smaller margin (0.1 to 0.2 J/m², for $n = 1$ and 4 in Table III). We now emphasize the fact that the incoherent interface model used for the calculation of $\tilde{\gamma}_{ML}$ is obviously unstable, as clearly seen in Figure 6 from the numerous high energy on-top positions. Upon relaxation

it is expected that a network of dislocation regions would form separated by regions which are similar to the most stable coherent interface, namely the one corresponding to the hollow sites. This would substantially increase the number of low energy terms corresponding to those hollow sites in the sum in Eq. 3. This essentially means that $\tilde{\gamma}_{ML}$ should be considered as an upper estimate for the excess energy of a relaxed semicoherent interface. It is also reasonable to assume that even if the excess interface energies are slightly underestimated, the resulting interface excess energy of a semicoherent (i.e., relaxed interface) is expected to offset any underestimation of gamma due to lateral strain. Hence the lateral strain in the coherent interface models is expected to have a negligible effect on the growth mode.

At last, we calculate $\tilde{\gamma}_{ML}$ following more closely the method of Benedek et al.⁴³ and show that both our and their methods are equivalent for $n = 1$. In Ref. 43 the contributions to the interface energy are approximately separated to either inter-phase (Cu-Ta) or intra-phase (Cu-Cu) interactions, where the intra-phase interactions are further decomposed into strain and relaxation contributions. The difference between the incoherent and coherent interface energies may be expressed as (see Eqs. (16) and (17) in Ref. 43):

$$\tilde{\gamma}_{ML} - \gamma_{ML} = \Delta\gamma_{intra}^{strain} + \Delta\gamma_{intra}^{rel} + \Delta\gamma_{inter} \quad (6)$$

where $\Delta\gamma_{intra}^{strain}$ is the strain energy, $\Delta\gamma_{intra}^{rel}$ is the relaxation energy contribution within the Cu film, and $\Delta\gamma_{inter}$ is the energy contribution due to the Cu-Ta interaction. In what follows, we shall neglect the intra-phase relaxation term $\Delta\gamma_{intra}^{rel}$, since it is expected to be small for a ML (for the case of an interface we already showed that full relaxation is much less than 1J/m²). By neglecting this term, $\tilde{\gamma}_{ML}$ becomes in effect an upper bound for the relaxed interface energy. For the inter-phase relaxation Benedek *et al.*⁴³ proposed the following form (using their original notation):

$$\Delta\gamma_{inter} = W_{h1} - \langle W \rangle \quad (7)$$

where, $W_{h1} \equiv W_{sep}^{ML}$ is the rigid work of separation of the most stable coherent state (corresponding in our case to the on hollow sites), and $\langle W \rangle = \tilde{W}_{sep}^{ML}$ is an effective work of separation for an incoherent interface, calculated in an equivalent manner to $\tilde{\gamma}_i$ in Eqs. (3) and (4) for $n = 1$. We also note that:

$$\gamma'_{ML} = \gamma_{ML} + \Delta\gamma_{intra}^{strain} \quad (8)$$

Combining Eqs. (6), (7), and (8), we obtain:

$$\tilde{\gamma}_{ML} = \gamma'_{ML} + W_{sep}^{ML} - \tilde{W}_{sep}^{ML} \quad (9)$$

substituting the values from Tables I, II, and III for W_{sep}^{ML} , $\tilde{W}_{sep}^{ML}$, and γ'_{ML} results in the incoherent effective interface energy: $\tilde{\gamma}_{ML} = 2.41\text{J/m}^2$. This is exactly

the same value as $\tilde{\gamma}_{ML}$ in Table II for $n = 1$. Hence, both our method and the method by Benedek et al.⁴³ result in the same effective interface energy of an incoherent interface for $n = 1$. In fact, it is straightforward to show that by substituting $W_{sep}^{ML} = \gamma_{Ta} + \gamma'_{Cu} - \gamma'_{ML}$ into Eq. (9), we obtain the same expression as presented in Eqs. (3) and (4). Hence, both methods are equivalent, although our method represented by Eqs. (3) and (4) is more straightforward to apply and provides means of a reasonable weighting.

IV. SUMMARY AND CONCLUSIONS

We have presented a first-principles DFT study of the mechanical and thermodynamic stability of the commensurate Cu(111)/Ta(110) interface in the Nishiyama-Wasserman orientation relationship for a thin Cu film and for a Cu ML on a Ta (110) substrate. Two structures for the thin film were considered, an fcc coherent Cu film and a bcc pseudomorphic Cu film. For the monolayer, two limiting cases were studied. In the first one the ML is pseudomorphic to the Ta bcc structure. This monolayer was found to be mechanically more stable than a thin film, but to be thermodynamically unstable, due to the strain energy in the Cu. The second limiting case is obtained when the Cu forms a commensurate and incoherent interface with the Ta. Using a simple energy-weighting scheme to estimate the work of separation and excess energy of the free incoherent Cu monolayer it is shown that a monolayer of Cu on Ta (110) can indeed be thermodynamically stable. Our results are therefore consistent with experimental data^{10–12} suggesting that a stable monolayer of Cu is formed on Ta. Our results resolve the discrepancy found in the literature¹³ pertaining to the dewetting of Cu film on Ta(110) by indicating that Cu dewets Ta but leaves a monolayer coverage. We have further shown that the Cu-Ta interface, both for a commensurate and a general interface would fail under tensile stress inside the Cu.

Although the scheme of our current study can't predict whether Cu would grow above the first monolayer in a 3D (SK) mode, the large strain in the Cu, as well as the wetting behavior of Cu on top of the monolayer strongly suggest an SK growth mode is most probably the preferred growth mode of Cu on Ta.

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