Atomic Structure and Work Function Modulations in Two-Dimensional Ultrathin CuI Films on Cu(111) from First-Principles Calculations

Giyeok Lee, Yun-Jae Lee, Krisztian Palotas, Taehun Lee,* and Aloysius Soon*

ABSTRACT: In electrochemical systems, upon applying an electrode potential, complicated surface reconstructions between halogen atoms (iodide anion) and the metal substrate (copper facet) have been observed from the ordered halide adlayers to ultrathin metal halide films. Although the global geometry of the ultrathin CuI film on Cu(111) was proposed, the local geometry is still not well-characterized, which is necessary to further explore its surface electronic structure. Thus, we performed van der Waals-corrected density functional theory calculations to examine the early stages of CuI ultrathin film formation on Cu(111) within the framework of ab initio (electrochemical) thermodynamics and report detailed surface atomic structures of the prepared ultrathin CuI films with their associated surface thermodynamics and simulated scanning tunneling microscopy images. Here, we find that due to the unique atomic arrangements in the ultrathin CuI film, the surface work function is uniquely influenced by pronounced charge transfer effects rather than polarization alone. These surface electronic effects are captured by analyzing the electronic charge density differences at the interfacial CuI layers. Finally, these results suggest that the surface work function is modulated by a competition between charge transfer and polarization, where the local surface structure determines their relative contributions.

INTRODUCTION

The presence of adsorbed anions in an electrochemical environment can significantly influence the electrochemical behaviors of a metal or alloy surface, such as in corrosion processes and catalytic reactions.1−3 In particular, halide anions are known to form strongly chemisorbed adlayers on metal electrode surfaces and subsequently ultrathin metal halide films upon increasing the electrode potential.4−6 Also, it has been reported that the halide adlayer (or ultrathin halide film) formation on metal surfaces is necessary to properly understand and predict surface work function modulations, which is strongly linked to the electrode potential of the metal electrode.7,8 There have been several computational9−12 and experimental studies13−14 to elucidate the structures of these surface halide overlayers and understand the physical origin of work function changes as a function of surface coverage of halide adsorbates (Θhalide).

A couple of studies have demonstrated the critical role of the Cu(111) surface in the growth of ultrathin CuI films.13−16 In 1982, DiCezon et al. discussed the correlation between the prepared surface structure of CuI thin films and γ-CuI(111) (where the zinc-blende γ-CuI phase is known to be the thermodynamic product among CuI polymorphs17,18 as illustrated in Figure 1a), emphasizing a heteroepitaxial growth of p(√5 × √3)R30° CuI on Cu(111) via low-energy electron diffraction (LEED) measurements.15 This observation was...
supported again by scanning tunneling microscopy (STM) studies, reporting that the iodine-adsorbed Cu substrate leads to the further growth of CuI layers under various preparation conditions.13,14,16

In particular, Hai et al. prepared well-ordered CuI films in an electrochemical environment.14 When the applied electrode potential was increased, different iodine-induced surface reconstructions occurred. At the low applied potential (−100 mV) with respect to a reversible hydrogen electrode (RHE), a \( p(\sqrt{3} \times \sqrt{3}) \) surface reconstruction with well-ordered iodide adlayer was captured by STM at a measured surface coverage of iodine atoms (\( \Theta_i \)) of 0.33 monolayer (ML).14 Interestingly, when higher positive potentials (from +80 to +120 mV) were applied, extreme surface reconstructions were observed. Note that the pre-existing iodine adsorbate layer \( p(\sqrt{3} \times \sqrt{3}) \) played the role of template for further growth of CuI bilayers. For the first step of Cu ultrathin film formation on the iodine-adsorbed Cu substrate, it was proposed that supersaturated mobile (CuI) monomers were formed by dissoluted copper ions from the step edges of the Cu substrate, bonding with the iodide anions in the electrolyte of the solution (e.g., potassium iodide, KI).14 Then, these monomers initiated nucleation and propagation of two-dimensional copper iodide islands. In their structural characterization, the measured apparent height of the prepared CuI films was 0.35 ± 0.015 nm with respect to the pre-existing iodine chemisorbed layer.14 Based on the analysis of the apparent height profile, Hai et al. proposed an atomic structure of the ultrathin film as a tristatic layer model where Cu atoms are sandwiched between I atoms, resembling the \( \gamma \)-CuI(111) surface (as shown in Figure 1b). Although the global geometry of the ultrathin CuI film was proposed, the local atomic structure remains unclear, e.g., whether the Cu atoms tetrahedra vertices are directed upward or downward toward the Cu(111) substrate in the out-of-plane direction. This atomic-scale information is critical (but yet unknown) to understand and interpret the surface work function changes in CuI/Cu(111).

To understand the surface work function changes (\( \Delta \Phi \)) of ultrathin CuI layers with respect to pristine CuI(111), the surface work function (\( \Phi \)) is computed via macroscopically averaging the electrostatic potential and taking the difference between the vacuum potential and the Fermi level. Then, to investigate the origin of \( \Delta \Phi \) of ultrathin CuI films, we split the surface dipole moment (\( \mu_{SD} \)) into two different terms, charge transfer (\( \mu_q \)) and polarization (\( \mu_{pol} \)), by adapting the theoretical framework of Groß et al.23 By integrating the one-dimensional charge density difference (\( \Delta \rho \)) along the \( z \) direction (see Equations S8–S10), we calculate \( \mu_{SD} \) and its components (\( \mu_q \) and \( \mu_{pol} \)) normalized by the surface area of the supercell.

## RESULTS AND DISCUSSIONS

### Structural Models of Ultrathin CuI Layers on Cu(111)

To resolve the atomic structure of ultrathin CuI layer on the Cu(111) substrate, we constructed CuI film structures in the monolayer regime based on the bonding character of bulk CuI polymorphs. Reflecting the experimental observation, \( p(\sqrt{3} \times \sqrt{3}) \) surface was used as a template/substrate layer.14–16 Indeed, the calculated lattice mismatch between \( p \) \((1 \times 1) \) \( \gamma \)-CuI(111) and the template, using the optB86b xc functional, is −3.39%, which is regarded as a rather small value compared to those of well-defined oxide/metal interface systems.

Our interface structures can be divided into three groups: The first one consists of on-surface adsorption models of iodine atoms on pristine CuI(111) with varying surface coverages of iodine (\( \Theta_i \)) ranging from 0.06 to 0.50 ML by increasing the supercell size of the CuI(111) substrate up to a \( p(4 \times 4) \) surface cell. For these structures, the adsorption strength of iodine adsorbates to the substrate was compared for I atoms placed at highly symmetrical adsorption sites,
namely the fcc-hollow (F), hcp-hollow (H), bridge (B), and top (T) sites. The second group includes ultrathin CuI structures that resemble the β-CuI{111} surface, varying the local direction of the vertex of the CuI$_4$ tetrahedron on the substrate and the number of stacked layers (ranging from one to three tetrahedral layers).

For the surface denotation, when the vertex of the CuI$_4$ tetrahedron is pointing toward the substrate, the structure is marked as $A_1$ when the vertex of the CuI$_4$ is oriented toward the vacuum region, it is termed as $B$, noting together with the number of tetrahedral units ($n = 1, 2, 3$) and adsorption sites (F, H, B, and T) of I atoms on the Cu(111) substrate. For example, H1LA denotes the interface structure composed of one inverted CuI$_4$ tetrahedron layer on the substrate where the bottom-most iodine atom of the CuI thin film is placed on the HCP hollow site of the substrate.

Lastly, the third group is motivated by the atomic structure of the β-Cu polymorph, which is a metastable rhombohedral phase existing between 390 and 440 °C. A recent theoretical high-throughput study on the discovery of two-dimensional materials has reported that the β-phase can be stable in its two-dimensional form with iodine terminations via a lattice dynamical analysis where the two-dimensional form is illustrated in Figure 1c. This exfoliable two-dimensional atomic structure can be understood as an interaction between CuI$_4$ trigonal pyramidal units normal to the surface and their inverted structures. Here, considering possible diversity at the interface, various atomic configurations of two tetrahedral units are included. The inverted (or upper) CuI$_4$ unit is stacked on the lower CuI$_4$ unit in various ways, applying rotational and translational symmetries.

The total number of surface structures considered in this work amounts to 78. The surface coverage of iodine ($\Theta_i$) and the atomic interlayer spacing of the selected (and optimized) surface structures are listed in Table S1. The structural properties of bulk γ-CuI and the exfoliable two-dimensional structure originated from the bulk β-CuI structural motif as well as the surface denotation of the third surface group are described in the Supporting Information.

**Surface Thermodynamics and Microscopy.** To understand the adsorption strength of iodine atoms of DFT-optimized surface structures, we computed the adsorption energy of iodine ($E_{ad}$) normalized by the number of iodine atoms as a function of the given surface coverage of iodine ($\Theta_i$) via Equation S1. In Figure 2, $E_{ad}$ is categorized into two groups where black (and gray) circular and red (and pink) rectangular symbols indicate $E_{ad}$ of on-surface adsorbate models until 0.50 ML of $\Theta_i$ and CuI ultrathin film models above $\Theta_i = 0.66$ ML, respectively.

At the low $\Theta_i$ condition, $E_{ad}$ of on-surface iodine adsorbate models becomes more negative until $\Theta_i$ becomes 0.33 ML (where $E_{ad} = -1.92$ eV), confirming the earlier experimental finding that the observed $\Theta_i$ of the iodine adsorbate at initial iodization condition was 0.33 ML. Well agreeing with the earlier calculations, the dramatic decrease of $E_{ad}$ in absolute value (highlighted by a black arrow) can be seen at 0.50 ML of $\Theta_i$ when $E_{ad} = -0.84$ eV due to the repulsive interaction of iodine atoms. As a result of the larger atomic radius of an iodine atom compared to that of a copper atom, iodine adsorbates at 0.50 ML of $\Theta_i$ structurally form double layers on the Cu(111) substrate. Thermodynamically, the binding strength of iodine adsorbates at 0.50 ML of $\Theta_i$ is weaker than that of other surface structures, which implies that this adsorbate structure dissociates into the other (thermodynamically more stable) ones near 0.50 ML of $\Theta_i$, such as to the on-surface adsorption model (0.33 ML of $\Theta_i$) or an ultrathin CuI layer (H1LA).

In previous theoretical studies on halogen atoms on Cu(111), the iodine-induced surface reconstructions beyond 0.50 ML of $\Theta_i$ have not been investigated, despite the evidence from several experimental works on the ultrathin CuI film formation. In our work, interestingly, when $\Theta_i$ increases up to 1.33 ML, $E_{ad}$ values of the ultrathin CuI interface structures (e.g., H1LA, H2LA, and H3LA) show more negative values than that of 0.50 ML by at least 0.11 eV. This indicates that under the chemically iodine-rich condition, it is naturally favorable to form ultrathin CuI layers from the iodine-chemisorbed template (when $\Theta_i$ is 0.33 ML). This result is in line with the experimental observation that the preadsorbed iodine layer at 0.33 ML of $\Theta_i$ plays a critical role in the further growth of CuI layers. During thin film growth, the lateral growth of the chemisorbed iodine is first observed, and with increasing $\Theta_i$ (when $\Theta_i \geq 1.33$ ML), ultrathin CuI layers will start to grow in the out-of-plane direction on the preadsorbed iodine layer. In particular, the preadsorbed iodine layer promotes the further growth of the CuI films in {111} orientation. We discuss their structural driving force later.

Figure 3 displays the results of Gibbs free energy of adsorption ($\Delta G_{ad}$) as a function of the change of the chemical potential of the iodine atom ($\Delta \mu_i$) (cf. Equation S2) with the illustrations of stable interface structures, namely 1$_{lm}$/Cu(111), H1LA, and H2LA at different iodine surface coverages of 0.33, 0.66, and 1.00 ML, respectively.

To understand the stability of interface structures under the experimental conditions, $\Delta \mu_i$ is expressed in terms of environmental factors that can be directly compared with the experimental conditions. Here, two different growth conditions are taken into consideration. First, $\Delta \mu_i$ is converted as a function of temperature (T) and partial pressure of the iodine gas ($p_i$) via Equation S3 because one of the common routes to prepare the ultrathin CuI films is to use chemical reactions in ultrahigh vacuum (UHV) with a vapor-phase iodide at the given temperature. As an alternative, the CuI films can
be prepared under an electrochemical condition, which is governed by the electrode potential \( (U) \) and pH of an electrolyte solution.\(^{14,35,36} \) Within an electrochemical thermodynamic framework, the chemical potential of an iodide anion \( (\mu_I) \) can be expressed as a function of \( U \) with respect to the standard hydrogen electrode (SHE) according to Equations S4 and S6. The reduction potential values of solvated iodide \((+0.54\, \text{V})\) and iodate \((+0.27\, \text{V})\) anions are taken from ref \(^{37}\). The theoretical approach, despite the fact that an electrical double layer is not explicitly considered, showed reasonably good agreements with relevant experiments.\(^{31,38} \) We refer the readers to the references\(^{23,33,34,40,41}\) for details of the theoretical approaches of (electrochemical) thermodynamics combined with \textit{ab initio} DFT energetics.

Now, we can compare the thermodynamic stability of ultrathin CuI layers on Cu(111) under the growth conditions to rationalize the experimentally observed global atomic geometry.\(^{14,36} \) Not surprisingly, our thermodynamic result (Figure 3a) shows that the on-surface adsorption model at 0.33 ML of \( \Theta_I \) \((\text{I}_I/\text{Cu}(111)) \) is the dominant phase in the majority of the energy window (from \(-1.92 \) to \(-0.62\, \text{eV of } \Delta\mu_I \)) due to the strong binding strength of the iodine adsorbate to the substrate (cf. Figure 2). In the optimized \( \text{I}_I/\text{Cu}(111) \) structure, the iodine atom sits at the HCP 3-fold hollow site, and this finding shows good agreement with earlier calculations.\(^{8,11} \) Moreover, when the iodine atom is adsorbed at the FCC 3-fold hollow site, the energy difference of \( \Delta G^{\text{ad}} \) with HCP 3-fold hollow site is only 0.001 eV/Å\(^2\). This indicates the possibility of coexistence of the on-surface iodine adsorbates at FCC and HCP 3-fold hollow sites on Cu(111).

The experimental preparation condition \((p_{\text{I}_2} = 2 \times 10^{-10}\, \text{Torr at } 298.15\, \text{K})\)\(^{13,16} \) is displayed in Figure 3a as a vertical dotted line \((\Delta\mu_I = -0.72\, \text{eV})\) with the corresponding pressure scale of iodide molecules at the bottom of the figure. At the given experimental condition, our calculation shows that \( \text{I}_I/\text{Cu}(111) \) is the most dominant phase, confirming the experimental observation of \( p(\sqrt{3} \times \sqrt{3})\)R30° reconstruction in UHV condition by Andryushechkin et al. in 2001.\(^{16} \)

In the same work,\(^{16} \) the authors observed thin CuI island growth on a chemisorbed iodine layer with a maximum height of 10 Å and its lateral size ranging from 10 to 500 Å. Near the experimental condition, the relative stability of interface structures is very competitive (see the inset of Figure 3a), which provides the possibility of the presence of metastable phases.\(^{41} \) At the given condition, if the \( \text{I}_I/\text{Cu}(111) \) structure is kinetically hindered, the thin CuI films such as H1LA, H2LA, and H3LA (or their structural relatives F1L A, B1LA, F2LA, B2LA, F3LA, and B3LA) might be the dominant phases due to the small energy difference with respect to the \( \Delta G^{\text{ad}} \) of \( \text{I}_I/\text{Cu}(111) \). Note that the averaged \( \Delta G^{\text{ad}} \) of \( \text{I}_I/\text{Cu}(111) \) and \( 3\lambda \) to that of \( \text{I}_I/\text{Cu}(111) \) are 0.009, 0.014, and 0.016 eV/Å\(^2\), respectively. Referring to the experimental observation by Andrushechkin et al.,\(^{16} \) although the structural details of the CuI islands (under 10 Å of the apparent height) have not been reported, the observed ultrathin CuI surface structures on Cu(111) might be H1LA or H2LA in the view of our thermodynamic and structural analysis (cf. the step height of surface structures in Table S1 of the Supporting Information).

Interestingly, the bonding character of the DFT-optimized interface structures H1LA, H2LA, and H3LA resembles that of the Cu(111) surface, conserving the CuI tetrahedral unit. Note that the \( \{111\} \) surface of the zinc-blende structure possesses two different surface orientations due to the lack of inversion symmetry along the \( \{111\} \) direction, resulting in \( \{111\} \) and \( \{111\} \) surfaces.\(^{42} \) In fact, the averaged bond lengths of CuI tetrahedra of H1LA, H2LA, and H3LA are the same, 2.64 Å within 2% difference to the corresponding value of the bulk phase, providing evidence of the structural correlation of those surfaces with the Cu(111) surface. However, unlike the surface structures originating from γ-Cul, the surface structures originating from β-Cul are unfavorable to form.

In addition, H1LA (possessing the downward CuI tetrahedron vertex toward the Cu(111) template) is much
more favorable than H1LB (in an opposite tetrahedron vertex configuration) by 0.047 eV/Å² of ΔG_{ad}, which resolves the experimental controversy on the local geometry of the CuI tetrahedron on Cu(111). To understand the structural driving force of the stabilization of the downward-oriented CuI tetrahedron, it is important to observe the bond length deviation between the outermost Cu atom of the substrate and the bottom-most iodine atom of the ultrathin film with respect to that of bulk γ-CuI. In fact, the iodine atom of the H1LA surface structure has four atomic bonds with Cu: three bonds with the substrate and another one with that of the ultrathin film, forming a pseudotetrahedron. The bond length between I and substrate Cu atoms is 2.69 Å, which shows only a +3.68% deviation with respect to that of the bulk structure (2.59 Å). Unlike the case of the H1L structure, the iodine atom of the H1L structure has a much more deviated bond length with respect to substrate Cu atoms, +9.80% compared to the Cu–I bond length in bulk.

Regarding the boundary condition of those thin films, thermodynamically, the ultrathin CuI layers cannot be formed when the value of Δμ_I is larger than the formation enthalpy of bulk γ-CuI normalized by the number of iodine atoms (ΔH_f-CuI = −0.73 eV) because bulk γ-CuI starts to form instead of the ultrathin films in the energy window. Above −0.73 eV of Δμ_I, a thicker thin film (H3L_A) can be stable with a steep gradient of ΔG_{ad} compared to the ultrathin layer in the monolayer regime (e.g., H1L_A). This implies that in the further iodization condition, CuI films thicker than monolayers are hard to form without the contribution of kinetics, thus explaining the experimental observations of the difficulty of the further growth of CuI thin films with high crystallinity.

Figure 3b shows the electrochemical Pourbaix diagram as a function of the electrode potential with respect to the standard hydrogen electrode (U_{SHE}) and pH values using Equation S4 and S6. At the negative electrode potential, the pristine Cu(111) surface is stable, not interacting with the iodide anion. At elevated potentials from 0.23 V, I/ Cu(111) becomes the dominant phase similarly as in the case of the UHV condition, taking the chemical reservoir of iodine from the iodide anion. The result is in line with the experimental observation of a p(√3 × √3)R30° surface reconstruction at low positive potential. Assuming the kinetic hindrance of the I/Cu(111) surface, at +0.91 V the H1L_A structure becomes stable which is originated from Γ regardless of the pH condition, confirming that the H1L_A is the experimentally observed ultrathin CuI structure on Cu(111). Also, in this process, as discussed in previous experimental work, the dissolved (solvated) copper ions in the electrolyte, might play a role to form ultrathin CuI layers via overcoming the thermodynamic barrier. At higher potentials, H3L_A can be stable with different chemical origins from Γ or IO_3^- at acidic and basic conditions (above +1.50 and +1.37 V), respectively. Despite the accurate identification of stable surface structures in comparison with the experiments, there is a discrepancy of our predicted electrode potential with the experimental values of each stable atomic configuration. We note that this discrepancy may arise from the current limitation of our theoretical model. For a more accurate description of the electrochemical Pourbaix diagram of ultrathin CuI layers, an explicit (or implicit) modeling of the proton, hydroxide ion, or other electrolyte ions in the thin film formation may be required, which is out of the scope of this current work. In particular, the adsorption of electrolyte ions on the surfaces might also alter the local surface chemistry, resulting in the stabilization of metastable surface structures.

Finally, regardless of the preparation conditions, our thermodynamic analysis (cf. Figure 3a and b) shows that I/Cu(111) is the thermodynamically dominant phase. In the further iodization condition, H1LA (and its thicker films), which structurally resembles CuI(111), can be formed with the help of kinetic hindrance.

To further confirm that the thermodynamically stable H1LA is the prepared thin film, we measure the interlayer spacing between the outermost layer of thin films and the bottom-most iodide adsorbate layer, and compare it with the experimental value (apparent height, 0.35 ± 0.015 nm) as illustrated in Figure 4a. Indeed, the measured step height of H1LA (3.34 Å) is within the error bar of the experimental value.

Using the constant current approach, the STM images of I/Cu(111) and H1LA are simulated at +14 and +200 mV bias voltages, in the right panel of Figure 4b and c, respectively. The relevant experimental STM images are adapted from ref 14 and displayed in the left panel of Figure 4b and c. Going beyond the simple Tersoff–Hamann approximation, we used the revised Chen’s method, which is implemented in the BSKAN code, where the electronic orbitals of a tip apex atom are taken into consideration. In our previous works, we demonstrated that the simulated STM images with the revised Chen’s method show better agreements with the relevant experiments. For the tip’s atomic configuration, a blunt tungsten tip functionalized with an iodine atom is employed. The functionalization of the tip apex is due to the adsorption of the iodine atom on the tip apex, which is structurally under-coordinated. For the details of the theoretical methodology, we refer our readers to refs 45 and 48.

Figure 4. (a) Interlayer spacing profile of ultrathin CuI layers on Cu(111) with the illustration of side view of the surface structures, I/Cu(111), H1LA, and H2LA. The orange and blue circles indicate copper and iodine atoms, respectively. Simulated STM images of the right panel of (b) I/Cu(111) at +14 mV and (c) H1LA at +200 mV, respectively, with overlaid surface structures of the outermost (b)layer. The experimental results of the corresponding simulated images are displayed at the left panel of (b) and (c). Reprinted with permission from ref 14. Copyright (2020) American Chemical Society.
Although the applied potential on the surface under electrochemical conditions may affect the experimental STM topographies due to the change in the Fermi level, the simulated STM images of I\_2/Cu(111) and H\_2I\_2A (in Figure 4b and c, in vacuum) seem to agree well with the reported experiments\(^\text{14}\) under electrochemical conditions. We deem the effect of the applied electrochemical potential bias on the simulated STM images to be negligible. The bright circular features of the STM images of I\_2/Cu(111) and H\_2I\_2A stem from the outermost iodine atoms. Note that regardless of the functionalization of the tip apex with iodine atoms, the simulated STM topographs result in the same bright features which are originated from iodine atoms (not shown in this work).

Finally, based on our surface characterizations from thermodynamic and microscopic views, it is obvious that the observed ultrathin CuI layers in previous experimental works\(^\text{14,14,30}\) are I\_2/Cu(111) and H\_2I\_2A in both the UHV and electrochemical environments. Moreover, H\_2I\_2A resembling γ-CuI(111) is a potentially good template for further growth of CuI surfaces just as the early stage of bulk oxide (namely, surface oxide), e.g., Cu surface oxide on Cu(111), which is structurally analogous to Cu\_2O(111).\(^\text{23,50}\)

**Surface Electronic Structures.** Turning our interest to the electronic properties of CuI/Cu(111) systems, we try to understand how the surface reconstructions impact on the electronic features. In general, on-surface adsorbed halogen atoms on metal substrates are known to increase the surface work function (Φ) by creating a surface dipole. However, an unexpected decrease of Φ by the adsorption of iodine atom was observed on Cu(111) surface.\(^\text{8,10}\) To understand the behavior of Φ induced by the adsorbate, the role of substrate charge polarization for I/Cu(111)\(^\text{10}\) and the surface spillover of electron charge into the vacuum for N/W(100)\(^\text{9}\) were discussed. The I/Cu(111) system was revisited in 2013 by Groß et al., and they showed that the reduced work function (or the almost linear change of work function as a function of iodine coverage) is a consequence of the canceling effects of the charge transfer from the substrate and the polarization induced by iodine adsorbates.\(^\text{8}\) It has also been discussed that a drastic jump of the work function at 0.50 ML of Θ\_i with respect to that of low Θ\_i by about 2 eV is caused by the creation of a dipole layer due to iodine double layers.\(^\text{8}\) Also, recent experimental advances make possible the measurement of the significant increase or decrease of the local surface work function by introducing the electron acceptor and donator adsorbates in ultrathin oxide films.\(^\text{31,52}\) It helps to disentangle the possible role of the charge transfer and surface polarization to the surface work function of thin oxide films on the metal substrate.

Interestingly, our thermodynamic results (cf. Figures 2 and 3) show that the formation of iodine double layers is not favorable compared to the ultrathin CuI films formation. Therefore, in the realistic picture, questions still remain about the influence of ultrathin CuI films formation on the surface work function, in comparison to the on-surface adsorption model, and the contributions of the electron charge transfer from the substrate and the surface polarization to the change of the work function.

To understand these fundamental questions, we plot the change of the surface work function (ΔΦ) of on-surface iodine adsorption models (from 0.06 to 0.50 ML of Θ\_i) and thermodynamically stable ultrathin CuI films (H\_2I\_2A, H\_2L\_2A, and H\_3L\_A) with respect to that of pristine Cu(111) by black circles and red squares, respectively, as a function of Θ\_i in Figure 5. Note that the calculated Φ of Cu(111) is 5.00 eV with optB86 xc functional, which is in good agreement with the previously reported theoretical value (4.78 eV)\(^\text{23}\) obtained with GGA-Perdew–Burke–Ernzerhof (PBE)\(^\text{35}\) xc functional as well as with the experiment (4.94 eV).\(^\text{34}\)

At low Θ\_i, ΔΦ shows small negative values exhibiting an almost linear behavior with the increase of Θ\_i until 0.33 ML. Interestingly, when Θ\_i = 0.33 ML (I\_2/Cu(111)), ΔΦ shows the lowest value of −0.22 eV (highlighted with an orange circle). There is a minute increase of ΔΦ at Θ\_i = 0.38 ML compared to 0.33 ML (from −0.22 to −0.04 eV). Then, due to the formation of the double iodine layers at 0.50 ML of Θ\_i this results in a significant increase of ΔΦ to 1.76 eV, which shows a good agreement with previous calculation.

Interestingly, CuI ultrathin layer formation (with the increase of Θ\_i) brings about the gradual increase of ΔΦ (that of H\_2I\_2A and H\_2L\_2A are 0.32 and 0.58 eV, respectively). However, the ΔΦ values of H\_2L\_2A and H\_3L\_A are almost the same, implying the saturation of ΔΦ. In Figure 5, the experimentally measured ionization potential (IP) using X-ray photoelectron spectroscopy (XPS) of the preferentially (111)-oriented CuI surface (5.4 ± 0.2 eV)\(^\text{31}\) is denoted with respect to the experimental value of Φ of Cu(111),\(^\text{54}\) i.e., IP\_cal = Φ\_Cu(111) (5.4 ± 0.2 eV), is denoted by a blue triangle symbol with the error bar. The solid line connecting the calculated values is a guide to the reader’s eye.
Our calculated $\mu_{SD}$ is in good agreement with an earlier calculation\textsuperscript{8} within 0.05 eV difference. Based on this approach, we calculated values of $\mu_{SD}$, $\mu_q$, and $\mu_{pol}$ with the optB86b xc functional, and the values are listed in Table S2 of the Supporting Information.

Figure 6a displays optB86b-computed $\mu_{SD}$ of on-surface iodine adsorption models (from 0.06 to 0.50 ML of $\Theta_l$) and thermodynamically stable ultrathin CuI films with black circles and red squares, respectively, as a function of $\Theta_l$. At low $\Theta_l$, $\mu_{SD}$ shows an almost linear feature with small positive values (up to +0.007 D/Å$^2$). As $\Theta_l$ increases to 0.50 ML, it results in a negative $\mu_{SD}$ (−0.048 D/Å$^2$) due to the negatively charged iodine atom in the outermost layer of the iodide double layer. For the ultrathin films beyond 0.50 ML of $\Theta_l$, such as H1L$_A$, H2L$_A$, and H3L$_A$, $\mu_{SD}$ shows negative values of −0.009, −0.016, and −0.015 D/Å$^2$, respectively, reflecting their positive $\Delta\Phi$.

We now discuss the contributions of $\mu_q$ and $\mu_{pol}$ to $\mu_{SD}$ (as shown in Figure 6b and c). It is obvious that the origin of the linear feature of $\Delta\Phi$ until 0.33 ML of $\Theta_l$ is due to the compensation between the polarization of the adsorbates and the charge accumulation from the substrate, in line with the previous calculation.\textsuperscript{8} In addition, the surface structure at 0.33 ML of $\Theta_l$ (see orange circle in Figure 6b) has the largest charge transfer ($\mu_q = -0.067$ D/Å$^2$) from the substrate to the adsorbate, which might be an electronic origin of the strong binding strength of iodine atom in I$_{1/2}$/Cu(111). In the ultrathin Cul films, the amount of charge transfer is fairly similar (−0.044 to −0.047 D/Å$^2$) regardless of the thickness of the surface structures. However, the surface dipole moment by the polarization of H1L$_A$ surface structure (+0.038 D/Å$^2$) is more positive than those of H2L$_A$ and H3L$_A$ (+0.028 to +0.029 D/Å$^2$), explaining the gradual increase of $\Delta\Phi$ from H1L$_A$ to H2L$_A$.

In the previous work on I/Cu(111),\textsuperscript{8} the role of the polarization induced by the adsorbate to the $\Delta\Phi$ behavior is emphasized because it determines the sign of $\Delta\Phi$ and overcompensates the net charge from the substrate. However, we realized that in the case of the thin films, the charge transfer plays a more critical role in the $\Delta\Phi$. Unlikely in the case of on-surface adsorbate models, the charge transfer of thin films from the substrate overcompensates the net polarization and finally governs the sign of $\Delta\Phi$ of thin films.

The insets of Figure 6b and c (cf. Figure S4) show the electron charge density difference ($\Delta\rho$) of I$_{1/2}$/Cu(111) and H1L$_A$, respectively, where the electron accumulation and depletion are denoted by red and blue colors. Our results show that there is a significant electron localization between the CuI (or iodine adsorbate) layer and the Cu(111) substrate regardless of the type of the surface structures, showing the significant electron accumulation in both I$_{1/2}$/Cu(111) and H1L$_A$ (see the arrow in the inset of Figure 6b). However, the surface reconstruction of the ultrathin films (e.g., H1L$_A$), forming Cu–I bonding chains in the outermost layer, results in an electron redistribution. Finally, it dramatically reduces the contribution of the surface polarization to the surface work function (as shown in the inset of Figure 6c). It provides further justification that the sign and magnitude of $\Delta\Phi$ of the ultrathin films are governed by $\mu_q$ rather than $\mu_{pol}$ as a result of the electron delocalization by surface reconstructions.

Finally, we conclude that the increase of the work function of ultrathin Cul films with respect to that of on-surface adsorbate surface structures is the consequence of the contribution of relatively enhanced charge transfer to polarization, quantifying the degree of charge transfer and electron redistribution. Our results also confirm the unique electronic property of the ultrathin layer H1L$_A$ compared to thicker films as well as to the bulk phase.

\section*{CONCLUSION}

In summary, we investigated the interfacial properties of thin Cul layers on Cu(111) substrate through first-principles DFT calculations. Our work revealed the stable atomic configurations of the ultrathin Cul layer on Cu(111) under the experimental conditions, providing a good agreement with the experimental measurement, e.g., scanning tunneling microscopy and step height of thin films. Moreover, our stable atomic
configuration in the monolayer regime shows strong structural correlation with the $\gamma$-CuI(111) surface. Based on surface dipole moment calculations, we explain the increase of the surface work function of the ultrathin CuI layer with respect to that of Cu(111). The saturation of the work function to the experimental value of the Cu surface is due to the contribution of relatively enhanced charge transfer from the substrate with respect to the polarization effect.

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c02842.

Detailed description of our theoretical methods; fundamental properties of ultrathin CuI layers and bulk Cu polymorphs; computed change of the surface work function ($\Delta\Phi$) and surface dipole moments ($\mu_{\text{SD}}$, $\mu_{\text{D}}$, and $\mu_{\text{pul}}$) of on-surface adsorbate models and ultrathin CuI layers; charge density difference plot ($\Delta\rho$) and its one-dimensional plot along the z axis ($\Delta\rho(1D)$) of on-surface adsorbate models and ultrathin CuI layers; change of the surface work function ($\Delta\Phi$) as a function of the applied potential (U) (PDF).

## Author Information

### Corresponding Authors

Taehun Lee — Department of Materials Science & Engineering and Center for Artificial Synthesis Materials Discovery, Yonsei University, Seoul 3722, Republic of Korea; orcid.org/0000-0002-5435-5910; Email: taehun0530@yonsei.ac.kr

Aloysius Soon — Department of Materials Science & Engineering and Center for Artificial Synthesis Materials Discovery, Yonsei University, Seoul 3722, Republic of Korea; orcid.org/0000-0002-6273-9324; Email: aloysius.soon@yonsei.ac.kr

### Authors

Giyook Lee — Department of Materials Science & Engineering and Center for Artificial Synthesis Materials Discovery, Yonsei University, Seoul 3722, Republic of Korea

Yun-Jae Lee — Department of Materials Science & Engineering and Center for Artificial Synthesis Materials Discovery, Yonsei University, Seoul 3722, Republic of Korea; orcid.org/0000-0003-0181-5351

Krisztián Palatás — Institute for Solid State Physics and Optics, Wigner Research Center for Physics, H-1525 Budapest, Hungary, MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, H-6720 Szeged, Hungary; orcid.org/0000-0002-1914-2901

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.0c02842

### Notes

The authors declare no competing financial interest.

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Supporting Information:

Atomic structure and work function modulations in two-dimensional ultrathin CuI films on Cu(111) from first principles

Giyeok Lee,‡ Yun-Jae Lee,‡ Krisztián Palotás,‡,¶ Taehun Lee,*† and Aloysius Soon*†

†Department of Materials Science & Engineering and Center for Artificial Synesthesia Materials Discovery, Yonsei University, Seoul 03722, Republic of Korea
‡Institute for Solid State Physics and Optics, Wigner Research Center for Physics, H-1525 Budapest, Hungary
¶MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, H-6720 Szeged, Hungary
E-mail: taehun0530@yonsei.ac.kr; aloysius.soon@yonsei.ac.kr
Methodology

Thermodynamics

To estimate how strongly iodine binds to the Cu(111) substrate, we define the adsorption energy ($E^{\text{ad}}$) (normalized by the number of the iodine atoms in the slab model) as

$$E^{\text{ad}} = \frac{1}{N_I} \left( E_{\text{CuI/Cu}} - E_{\text{Cu(111)}} - \Delta N_{\text{Cu}} E_{\text{Cu}} - \frac{N_I}{2} E_{\text{I}_2} \right), \quad (S1)$$

where $E_{\text{CuI/Cu}}$, $E_{\text{Cu(111)}}$, $E_{\text{Cu}}$, and $E_{\text{I}_2}$ are DFT-calculated total energies of the iodine-reconstructed slab, the clean Cu(111) substrate, bulk copper, and iodine molecule, respectively. $\Delta N_{\text{Cu}}$ and $N_I$ denote the change of the number of copper atoms and the number of iodine atoms to form ultrathin CuI layers, accordingly.

Using *ab initio* (electrochemical) thermodynamic approaches, we compute the Gibbs free energy of adsorption ($\Delta G^{\text{ad}}$) of ultrathin CuI surface halide layers as a function of the atomic chemical potential of copper and iodine ($\mu_{\text{Cu}}$ and $\mu_I$) by

$$\Delta G^{\text{ad}} \approx \frac{1}{N_I} \left( G_{\text{CuI/Cu}} - G_{\text{Cu(111)}} - \Delta N_{\text{Cu}} \mu_{\text{Cu}} - N_I \mu_I \right), \quad (S2)$$

where $G_{\text{CuI/Cu}}$ and $G_{\text{Cu(111)}}$ are Gibbs free energies of the iodine-reconstructed slab and the clean Cu(111) substrate, respectively. The chemical potential of Cu is chosen as the DFT energy of a Cu atom in bulk Cu.

To predict the stable atomic configuration of surface structures under ultra-high vacuum (UHV) conditions, $\mu_I$ is expressed in terms of the partial pressure of the I$_2$ gas molecule and the given temperature ($T$) as

$$\mu_I(T, p) = \frac{1}{2} E_{\text{I}_2} + \Delta \mu_I(T, p^0) + \frac{1}{2} k_B T \ln \left( \frac{p}{p^0} \right), \quad (S3)$$

where $p$ and $p^0$ are the partial and the standard pressures of the I$_2$ molecule respectively.\textsuperscript{1–4}
\( \mu_1(T, p) \) is treated with respect to half the energy of an iodine molecule (\( \Delta \mu_1 = \mu_1 - E_{1/2}^{mle} / 2 \)).

Employing \textit{ab initio} electrochemical thermodynamic approaches, as proposed by Rossmeisl \textit{et al.}\(^5\) and revised by Groß \textit{et al.},\(^6-9\) the influence of the electrode potential (\( U \)) is considered via reformulating the chemical potential change of the adsorbate (iodine atom) in solution with respect to the standard hydrogen potential (\( \Delta U_{\text{SHE}} \)). Here, the chemical potential (\( \tilde{\mu} \)) of the adsorbate at the standard state (\( T = 298 \) K and \( p = 1 \) bar) is \( \mu + neU \), where \( e \) and \( n \) are taken as the elementary charge and the charge of the species, respectively.

In this study, the chemical potential of the iodide anion, is thus expressed as a function of \( \Delta U_{\text{SHE}} \) under electrochemical conditions,\(^10-12\)

\[
\tilde{\mu}_1(\text{I}^-) = \tilde{\mu}_{1^-} - \tilde{\mu}_{e^-} = \mu_1^{\circ} + e(U_{\text{SHE}} - U_1^{\circ}) + RT\ln([\text{I}^-]) , \quad (S4)
\]

where \( \tilde{\mu}_{1^-} \) and \( \tilde{\mu}_{e^-} \) are the chemical potentials of the iodide anion and the electron in the solution environment, respectively. \( \mu_1^{\circ} \) is the chemical potential of iodide anion at the standard state (298.15 K and 1 mol/L), and the reduction potential of the iodide anion (\( U_1^{\circ} \)) is taken as a listed value (+0.54 V).\(^13\) Here, \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)).

Here, we assume that not only iodide anions, but also iodate ions (\( \text{IO}_3^- \)) participate in the formation of the CuI ultrathin film, in accordance to the measured Pourbaix diagram of iodine species reporting the presence of \( \text{IO}_3^- \) at the positive electrode potential.\(^14\) To reflect this in our surface electrochemical stability prediction, we first obtain the relationship between \( \text{I}^- \) and \( \text{IO}_3^- \) under equilibrium conditions (i.e. \( \text{I}^- + 6\text{OH}^- \leftrightarrow \text{IO}_3^- + 3\text{H}_2\text{O} + 6e^- \)).\(^15,16\) We next establish the relationship between the chemical potentials of \( \text{I}^- \) and \( \text{IO}_3^- \) as

\[
\tilde{\mu}_{1^-} + 6\tilde{\mu}_{\text{OH}^-} = \tilde{\mu}_{\text{IO}_3^-} + 3\tilde{\mu}_{\text{H}_2\text{O}} + 6\tilde{\mu}_{e^-} , \quad (S5)
\]

where \( \tilde{\mu}_{\text{OH}^-} \) and \( \tilde{\mu}_{\text{IO}_3^-} \) are the chemical potentials of the hydroxide and iodate ions, respectively. \( \mu_{\text{H}_2\text{O}}^{\circ} \) is the chemical potential of water molecule under the standard conditions.

Finally, \( \tilde{\mu}_1 \) can be re-expressed by taking the iodate ion as the chemical reservoir of the
ultrathin CuI layers:

$$\tilde{\mu}_I(\text{IO}_3^-) = \mu_{\text{IO}_3^-}^o + 3\mu_{\text{H}_2\text{O}}^o - e(5U_{\text{SHE}} - 6U_{\text{IO}_3^-}^o + U_{\text{I}}^o) + R\ln([\text{IO}_3^-]) - 6RT\ln(10)pH \ , \ (S6)$$

where $\mu_{\text{IO}_3^-}^o$ is the standard chemical potential of iodate ion, and $U_{\text{IO}_3^-}^o$ is the standard reduction potential of iodate ion (+0.27 V), respectively. The concentrations of iodide ([I$^-$]) and iodate ([IO$_3^-$]) ions are both set to 10$^{-6}$ mol/L. The values of $\mu_{\text{I}}^o$, $\mu_{\text{IO}_3^-}^o$, and $\mu_{\text{H}_2\text{O}}^o$ are taken from the experiments as $-0.59, -2.29, -2.46$ eV/f.u., respectively.

**Surface dipole moment**

To understand the surface work function changes ($\Delta \Phi$) of ultrathin CuI layers with respect to pristine Cu(111), the surface work function ($\Phi$) is computed via macroscopically averaging the electrostatic potential and taking the difference between the vacuum potential and the Fermi level.

For the CuI/Cu(111) interface structures, the electron charge density difference ($\Delta \rho(r)$) between the Cu and I atoms in the ultrathin CuI layer and Cu(111) substrate is defined as

$$\Delta \rho(r) = \rho_{\text{CuI/Cu}}(r) - \rho_{\text{Cu}}(r) - \rho_I(r) - \rho_{\text{Cu}(111)}(r) \ , \ (S7)$$

where $\rho_{\text{CuI/Cu}}(r)$, $\rho_{\text{Cu}}(r)$, $\rho_I(r)$, and $\rho_{\text{Cu}(111)}(r)$ are the electron densities of the interface (CuI/Cu(111)), isolated Cu and I atoms in the ultrathin CuI layer, and bare Cu(111), respectively.

Earlier calculations show how the surface work function can be altered by the introduction of a halogen adsorbate atom on pristine transition metal surfaces, as explained by analyzing the surface dipole moment ($\mu_{\text{SD}}$). Here, following that approach, we discuss the influence of (i) charge transfer from the substrate and (ii) polarization of the thin film, on the surface dipole moment, which determines the magnitude of the surface work function.

To calculate $\mu_{\text{SD}}$ of surface structures, the one-dimensional electron charge density differ-
ence profile ($\Delta \rho^{1D}$) along the z direction is obtained by a lateral summation of the difference electron charge density, $\Delta \rho(r)$ at each $x$ and $y$ position, noting that the zero value of z axis is set at the position of (averaged) outermost Cu atoms of the substrate. Finally, the total surface dipole moment of the slab, ($\mu_{SD}$ in Debye unit) normal to the surface is obtained as

$$\mu_{SD} = - \int_{\text{bulk}}^{\text{vac}} z \Delta \rho^{1D}(z) dz \quad , \quad (S8)$$

where $z \Delta \rho^{1D}(z)$ is integrated from the bulk-like region to the vacuum of the slab model, noting that the negative and positive sign of $\Delta \rho^{1D}$ stands for electron accumulation and depletion, respectively. To understand the contribution of the charge transfer from the metal substrate to ultrathin layers to $\mu_{SD}$, the charge transfer term ($\mu_q$) is calculated as

$$\mu_q = - \bar{z}_X \int_{z_q}^{\text{vac}} \Delta \rho^{1D} dz \quad , \quad (S9)$$

where $\bar{z}_X$ is the averaged position of the iodine atoms of ultrathin CuI layers adjacent to the Cu(111) substrate, and $z_q$ is the $xy$ plane where $\Delta \rho^{1D}$ changes from electron depletion to accumulation between the outermost substrate Cu atoms and the iodine atoms of the ultrathin CuI film, assuming the maximum charge transfer from the substrate. Finally, we disentangle the surface dipole moment ($\mu_{SD}$) into the charge transfer term ($\mu_q$) and the contributions from polarization ($\mu_{pol}$) based on Equations S8 and S9 by

$$\mu_{SD} = \mu_q + \mu_{pol} \quad . \quad (S10)$$

We have checked the convergence of surface dipole moment values by increasing FFT grids up to four times with respect to the cut-off vector, $G_{\text{cut}}$ with a convergence criteria of $\pm 0.001 \, \text{D/Å}^2$.  

S5
**Bulk $\gamma$-CuI**

The $\gamma$-phase of CuI is known as a thermodynamic product at the ambient condition among the various polymorphic phases of bulk CuI. The $\gamma$-phase has a zinc-blende (B3) structure (with a space group $F\bar{4}3m$ and the cubic crystal system). The zinc-blende structure can be explained as the occupation of the half tetrahedral interstitial sites in a face-centered cubic system, which results in the local tetrahedron (here, CuI$_4$) where each cation (or anion) is located at the center of the tetrahedron (forming four Cu-I bonds). Our computed lattice constant of $\gamma$-CuI is 6.00 Å with optB86 $xc$, which shows good agreement with experiment (6.05 Å) and other theoretical results (6.09 Å and 6.07 Å), respectively. Our computed bandgap of $\gamma$-CuI with HSE06 hybrid functional at the optB86-optimized structure is 2.64 eV which is in agreement with the previous theoretical work (2.59 eV) computed with HSE06 $xc$ functional.

![Projected density-of-states (PDOS) of bulk $\gamma$-CuI with Cu 3$d$, 4$s$ and I 5$p$, 5$s$ states with the illustration of the atomic structure. The Fermi energy is denoted by the vertical dashed line at 0 eV. The orange and blue circles denote Cu and I atoms, respectively.](image)
Two-dimensional form of CuI and its surface denotation

The third group of considered surface structures is motivated by the atomic structure of β-CuI polymorph, as discussed in the main manuscript. This exfoliable two-dimensional form is originated from bulk β-CuI. The DFT-calculated lattice constant of this exfoliated surface structure is 4.09 Å and 7.12 Å for $a_0$ and $c_0$ with a space group $P\bar{3}m1$, respectively. The computed lattice mismatch of the exfoliated surface to $p(\sqrt{3} \times \sqrt{3})R30^\circ\text{Cu(111)}$ is $-6.84\%$. The calculated bandgap of this structure with HSE06 hybrid functional is 3.28 eV.

Here, we outline how to denote surface structures motivated by a two-dimensional form of β-CuI polymorph (simply ‘2D’). First, the binding sites of iodine atom of bottom-most layer on Cu(111) substrate are denoted by F, H, B, and T, which follow the same rule as other surface structures discussed in the main manuscript. Secondly, $i$ stands for the inverted direction of the top layer. Lastly, the applied translational and rotational symmetries of the top CuI$\text{3}$ layer with respect to the position of the bottom CuI$\text{3}$ layer are denoted; the stacking of the top layer can be translated to the bottom layer as $t_1(0, 0)$, $t_2(1/3, 1/3)$ and $t_3(2/3, 2/3)$ vectors with respect to $p(\sqrt{3} \times \sqrt{3})R30^\circ\text{Cu(111)}$; the top layer can be rotated by 60° compared to the bottom layer (marked as $r60^\circ$).
Table S1: The interlayer spacing between the outermost layer of ultrathin CuI and the previous iodine adsorbate layer on $p(\sqrt{3} \times \sqrt{3})R30^\circ$ Cu(111) substrate in comparison with the experimentally reported step height ($0.35 \pm 0.015 \text{nm}$)$^{23}$ with surface iodine coverage ($\Theta_I$).

| $\Theta_I$ (ML) | Surface       | Spacing (Å) | Difference with expt. (Å) |
|----------------|---------------|-------------|--------------------------|
| 0.33           | $I_H$/Cu(111) | 2.22        | -                        |
| 0.66           | H1L$_B$       | 3.39        | -0.11                    |
| 0.66           | H1L$_A$       | 3.34        | -0.16                    |
| 0.66           | H2D$+t_3$     | 3.48        | -0.02                    |
| 0.66           | T2D$_i$ + $t_1$ | 3.86       | +0.36                    |
| 0.66           | T2D$_i$ + $t_1 + r60^\circ$ | 3.48 | -0.02   |
| 0.66           | T2D$_i$ + $t_2$ | 3.46       | -0.04                    |
| 0.66           | T2D$_i$ + $t_2 + r60^\circ$ | 3.61 | +0.11   |
| 0.66           | T2D$_i$ + $t_3$ | 3.34       | -0.16                    |
| 0.66           | T2D$_i$ + $t_3 + r60^\circ$ | 3.68 | +0.18   |

| 1.00          | H2L$_B$       | 6.75        | -                        |
| 1.00          | H2L$_A$       | 6.72        | -                        |
| 1.33          | H3L$_A$       | 10.09       | -                        |

*Interlayer spacing between outermost Cu atom of substrate and iodine adsorbate atom*
Table S2: Computed work function ($\Phi$), the change of the work function with respect to the pristine Cu(111) surface ($\Delta\Phi$), the total surface dipole moment normalized by areas ($\mu_{SD}$) and the number of iodine atom ($\mu_N$), and the components of $\mu_{SD}$ (the term of the charge transfer from the metal substrate to the ultrathin layers, $\mu_q$ and the polarization effect, $\mu_{pol}$) for the on-surface iodine adsorption models and ultrathin CuI layers on Cu(111) with $\Theta_I$, using optB86b xc functional.

| Surface               | $\Theta_I$ (ML) | $\Phi$ (eV) | $\Delta\Phi$ (eV) | $\mu_{SD}$ (D/Å$^2$) | $\mu_q$ (D/Å$^2$) | $\mu_{pol}$ (D/Å$^2$) | $\mu_N$ (D) |
|----------------------|-----------------|-------------|-------------------|----------------------|------------------|------------------------|-------------|
| Cu(111)              | -               | 5.00        | -                 | -                    | -                | -                      | -           |
| 1/16                 | 0.06            | 4.85        | -0.15             | +0.004               | -0.004           | +0.008                 | +0.318      |
| 2/16                 | 0.13            | 4.81        | -0.19             | +0.005               | -0.010           | +0.015                 | +0.230      |
| 3/16                 | 0.19            | 4.81        | -0.19             | +0.004               | -0.020           | +0.024                 | +0.121      |
| 4/16                 | 0.25            | 4.82        | -0.18             | +0.005               | -0.030           | +0.035                 | +0.108      |
| 6/16                 | 0.38            | 4.96        | -0.04             | +0.000               | -0.057           | +0.057                 | +0.004      |
| 8/18                 | 0.50            | 6.76        | +1.76             | -0.048               | -0.029           | -0.019                 | -0.530      |
| $I_H$/Cu(111)        | 0.33            | 4.77        | -0.23             | +0.007               | -0.067           | +0.074                 | +0.108      |
| H1L$_A$              | 0.67            | 5.31        | +0.31             | -0.009               | -0.047           | +0.038                 | -0.077      |
| H2L$_A$              | 1.00            | 5.58        | +0.58             | -0.016               | -0.044           | +0.028                 | -0.091      |
| H3L$_A$              | 1.33            | 5.58        | +0.58             | -0.015               | -0.044           | +0.029                 | -0.064      |
Figure S2: One-dimensional charge density difference ($\Delta \rho^{1D}(z)$) of (a) on-surface iodine adsorption models varying $\Theta_1$ from 0.06 to 0.50 ML and (b) ultrathin CuI layers (namely, $I_{H}/Cu(111)$, $H1L_A$, $H2L_A$, and $H3L_A$). $\Delta \rho^{1D}$ is normalized by surface area of the slab model.

Figure S2b shows one-dimensional electron charge perturbation along the $z$ axis ($\Delta \rho^{1D}$, cf. Equation 8) of the ultrathin layers ($H1L_A$, $H2L_A$, and $H3L_A$). It can be seen that the degree of the electron charge (or electron spillover) oscillation near the outermost layer as well as at the structural gap (between the substrate and the ultrathin layers) decreases with respect to that of the on-surface adsorption model at 0.33 ML of $\Theta_1$. 

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Figure S3: Calculated surface dipole moment ($\mu_{SD}$) as a function of $\Theta_I$ using PBE $xc$ functional (black circles). The reference values blue (triangles) are taken from Reference 18 to validate our methodology.

Figure S4: Charge density difference of (a) I$_{H}$/Cu(111), (b) H1L$_{A}$, and (c) H2L$_{A}$. Electron accumulation and depletion is denoted by red and blue color, respectively (the value of isosurface is $\pm 0.0025 \text{e/Å}^3$). The positions of Cu atoms in the outermost substrate layer, iodine and Cu atoms of ultrathin CuI layers are denoted by black, blue, and orange circles, respectively.
Figure S5: The change of the surface work function ($\Delta \Phi$) of the stable surfaces with respect to pristine Cu(111) as a function of the applied potential ($U$), at $p\text{H} = 7$. The solid red line and dotted red line indicate stable and metastable phases at the given conditions, respectively.
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