

Adhesion of thin metallic layers on Au surfaces

Linda A Zotti^{1,*}  and David D O'Regan² 

¹ Departamento de Física Teórica de la Materia Condensada and IFIMAC, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

² School of Physics, AMBER and CRANN Institute, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland

E-mail: linda.zotti@uam.es

Received 4 February 2022, revised 7 April 2022

Accepted for publication 19 April 2022

Published 6 May 2022



Abstract

We carried out first-principles density-functional theory calculations to study the work of separation for five different metal–metal interfaces, each of them comprising thin layers of selected metals (Cr, W, Ta, Al or Ti) lying on top of Au surfaces. We found that the highest work of separation is obtained for one-atom-thick layers. Increasing the number of atomic layers leads the work of separation to oscillate with the thickness, and ultimately tend to a limiting value for a large number of layers. Interestingly, for most cases the lowest work of separation is obtained for two-atom layers. We find that this behaviour is mirrored by the quantity of charge transferred between the two metals on the one hand, and their spatial distance on the other.

Keywords: metallic interfaces, DFT, work of separation, thin metallic adlayers

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Learning to control the stability of metallic interfaces is important for a number of applications in industry, including transistors, catalysis and reflectors, as well as for the development of solders, heat-dissipation problems in electronic devices, friction, lubrication, manipulation of material properties, plasmonics and mirrors [1–11]. Various physical factors need to be taken into account, such as the orientation of the crystal structure, magnetism, electronic, mechanical and thermodynamic properties [12–20]. A key property that has been found to be critical for adhesion is the layer thickness. For instance, increasing amount of wetting material can cause its diffusion into the substrate lying underneath, and it can also

result into occupied electronic states being shifted towards the Fermi level [3, 21]. Furthermore, as shown in reference [22], for layers of Cr, W, Ta, Al and Ti deposited on Au, it was found that the dewetting half-life under laser irradiation decreased, remarkably, with increasing layer thickness.

These and other recent experiments have elucidated the role of thickness in metallic interfaces at the level of nanometers, which is the range of main interest for industrial applications [20, 22]. However, little is known about adhesion at the level of atomically-thick layers, where interesting physics is expected to arise due to quantum effects [23]. In this work, we aim to begin to fill this knowledge gap, by means of quantum-mechanical calculations. Specifically, we present a computational study on ultra-thin metallic films consisting of a very few atomic layers lying on top of a metal surface, with the aim of understanding what factors determine the energetics and robustness of these kinds of systems. To this end, we built five interfaces obtained by matching a Au slab with thin layers of Cr, W, Ta, Al and Ti. This choice was inspired by the

* Author to whom any correspondence should be addressed.



Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](#). Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

forementioned experiments reported in reference [22] but is also very convenient from a theoretical perspective: it allows us to identify trends arising from the common bcc crystal structure exhibited by Cr, W, and Ta, while checking, at the same time, whether they can also be observed with different crystal structures such as the fcc or hcp configurations of Al and Ti, respectively.

One of the quantities which can be used to evaluate the stability of an interface is the work of separation, which is the energy (per unit area) required to split the interface into two surfaces [17, 24–33]. We will indeed focus on this quantity and investigate its dependence on the adlayer thickness. Interestingly, our results will not show a monotonic relationship, as naïvely expected, but rather an oscillatory behaviour, with amplitude decreasing with thickness. Oscillations were previously observed in experimental measures of adhesive forces of Pb on Si surfaces [7]. Nevertheless, to the best of our knowledge, from a first-principles theoretical perspective oscillations have only been analysed in the surface energies of individual metallic surfaces, without extending the investigation to their occurrence in interfaces [23, 34–37].

2. Results and discussion

We built metal–gold–metal interface models in which a central gold slab consisting of 13 layers is contained between two metallic films of one- to seven-atom-thickness (figure 1). Such symmetric structures were set up so as to avoid any possible artefacts deriving from the formation of spurious dipoles. For the adlayers, we chose Cr(100), W(100) and Ta(100) (all of them bcc), as well as Al(100) (fcc) and Ti(0001) (hcp) for comparison purposes. The reason for the crystal orientation adopted in each interface is provided in the methods section. As for the specific metals, as mentioned above, this choice (which was inspired by reference [22]) will allow us to understand whether any common trends identified within the bcc set can be extrapolated to metals of different crystal structures.

As explained in the methods section, in our calculations unit cells contained only one atom in the xy plane (parallel to the interface). The work of separation per atom was evaluated (noting that periodicity is applied in all directions) as

$$W(E_{\text{metal-vacuum-Au-vacuum-metal-vacuum}} - E_{\text{metal-Au-metal-vacuum}})/2. \quad (1)$$

Here, $E_{\text{metal-Au-metal-vacuum}}$ is the energy of the metal–Au–metal system under study as that shown in figure 1 (with metal $M = \text{Cr, W, Ta, Al, Ti}$), while $E_{\text{metal-vacuum-Au-vacuum-metal-vacuum}}$ is the energy of the system in which both metal adlayers are kept at a distance of about 10 Å from the Au slab. The size of the unit cell was the same in both calculations. The factor 2 in equation (1) takes into account the presence of two identical interfaces inside the system. To corroborate the robustness of this approach, we also calculated, for a few selected cases, the work of separation using the same method as in references [17, 27], where it was evaluated as the difference between the energy of the combined system and the sum of the energies of the

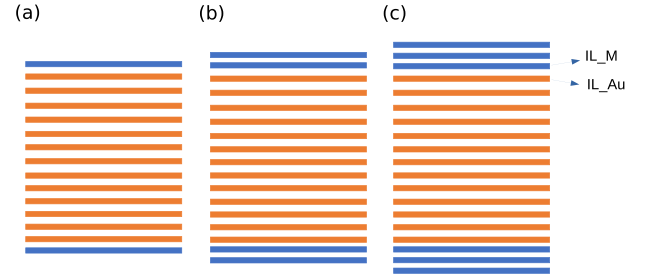


Figure 1. Schematic representation of the metal–Au–metal structures with adlayers of one to three-atom thicknesses. For the last case, the IL-Au and IL-M are indicated, where IL denotes interface layer.

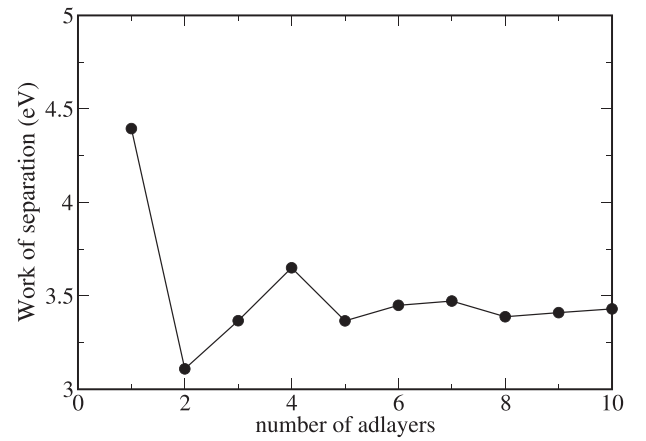


Figure 2. Work of separation (per atom) for the Ta–Au–Ta interface as a function of number of layers on each side of the junction.

individual slabs. We found very little discrepancy between the two methods, with a difference in energy of 0.02–0.04 eV.

We first analysed the Ta–Au interface as it was found to be one of the most stable systems in both the computational simulations of reference [24] and the experimental observations of reference [22]. In figure 2, we show the work of separation obtained by interfacing 1-to-10 Ta layers with the 13-layer Au slab, on both sides. We observe that strong work of separation oscillations with layer count are observed up to five layers on each side. Beyond this, their amplitude decreases with increasing number of layers. We believe that this effect is unlikely to be detected in standard experiments, where the thickness of the thinnest layers considered is usually larger than a few atoms (although it is worth noting that experiments on Pb islands on Si described in reference [7] showed oscillations of adhesive forces in the range of 14 monolayers). Computational studies on surface energies of individual surfaces [23, 34–37] showed oscillations that were attributed to quantum size effects and quantum well states. Given that the work of separation is strongly related to surface energies [24], it is thus perhaps not too surprising that the former reveals a similar behaviour. Nevertheless, it is possible to gain insight in such oscillations by investigating the corresponding changes in the geometrical structure and in the electronic configurations. To this end, we will focus on the interfaces comprising one-, two- and three-atom-thick adlayers, where the stronger variations

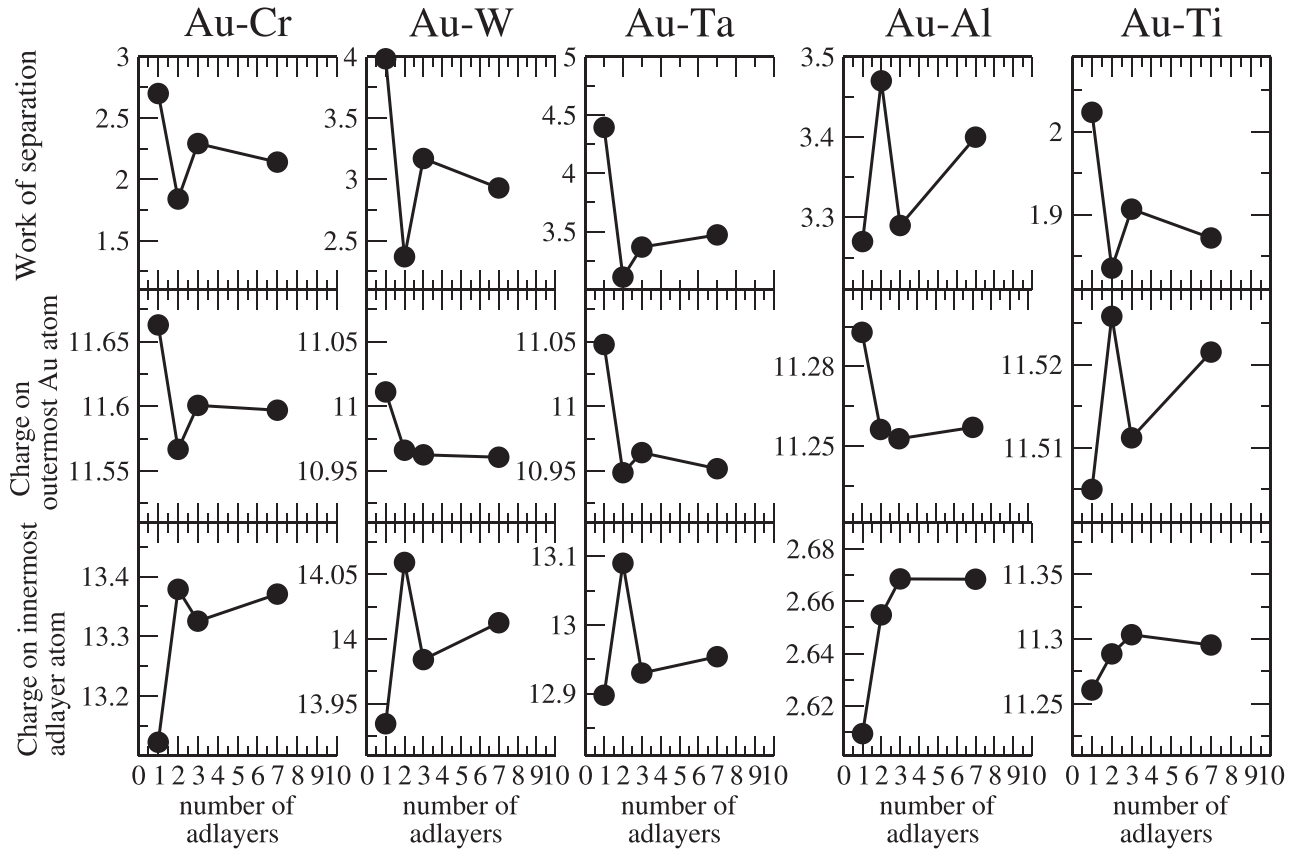


Figure 3. Work of separation (top row), absolute pseudoatomic Löwdin charges on the IL-Au atom (middle row) and on the IL-M adlayer atom (bottom row). The bulk values for the Löwdin charges on Au, Cr, W, Ta, Al and Ti, are 10.99, 13.75, 13.99, 12.99, 2.95 and 11.70, respectively.

are observed. For comparison purposes, we will also consider interfaces including seven-atom-thick adlayers, for which the oscillations shown in figure 2 already appear to be significantly damped. Accordingly, we will analyse similar sets for the interfaces incorporating the other four metals considered in this study.

In the top row of figure 3, we show the work of separation for all five systems and for all four-layer combinations employed. We observe that Au–Cr, Au–W and Au–Ti show similar trends to that of Au–Ta, with the highest and lowest work of separation being predicted for 1 and 2 adlayers, respectively. It is worth mentioning that higher stability for thinner than for larger adlayers was also observed in reference [22], although the experimental results there reported cannot be directly compared with ours because they were obtained with much thicker layers. Furthermore, certain restrictions and assumptions are imposed in our calculations that do not necessarily apply to the same experimental conditions (vide infra). Figure 3 also reveals that the work of separation for the Au–Al shows quite a different trend with respect to the others. However, its values oscillate within a very narrow range (0.2 eV) as compared to wide range covered by the other metals (up to 2 eV). We ascribe this difference to the fact that Al is the only *p* metal amongst the five metals interfaced with Au in the present work. We will come back to this point further ahead.

In the middle row of figure 3, we show the pseudoatomic Löwdin charges in the Au atom at the interface (which will be henceforth referred to as IL-Au), that is the layer in direct contact with the adlayer. We will first focus on the interfaces incorporating the three bcc metals, i.e., Cr, W and Ta. Note that, although the overall charge transfer takes place from bcc to fcc [24], in some cases Friedel (possibly in combination with orbital orthonormalisation) oscillations cause the valence electron count on this specific Au atom to be lower than the bulk value (10.99). Likewise, the charge in the IL-M bcc atom is, in certain cases, higher than the corresponding bulk value despite the aforementioned charge-transfer direction. The charges along the whole junction are reported in figure S1 (<https://stacks.iop.org/JPCM/34/275001/mmedia>) of the supporting information. Interestingly, in figure 3 we observe that, in the case of Au–Cr and Au–Ta, the trend shown by the charge in the IL-Au atom across the number of adlayers is similar to that of the work of separation. This also applies to Au–W, except for the drop at two layers which appears in the work of separation but not in the charge of that Au atom, and which demonstrates that there are effects beyond charge transfer at play simultaneously in the formation of the work of separation oscillations.

The third row of figure 3 shows the charge on the adlayer atom in direct contact with gold (which will be henceforth called IL-M). It is lower for one adlayer, as opposed to

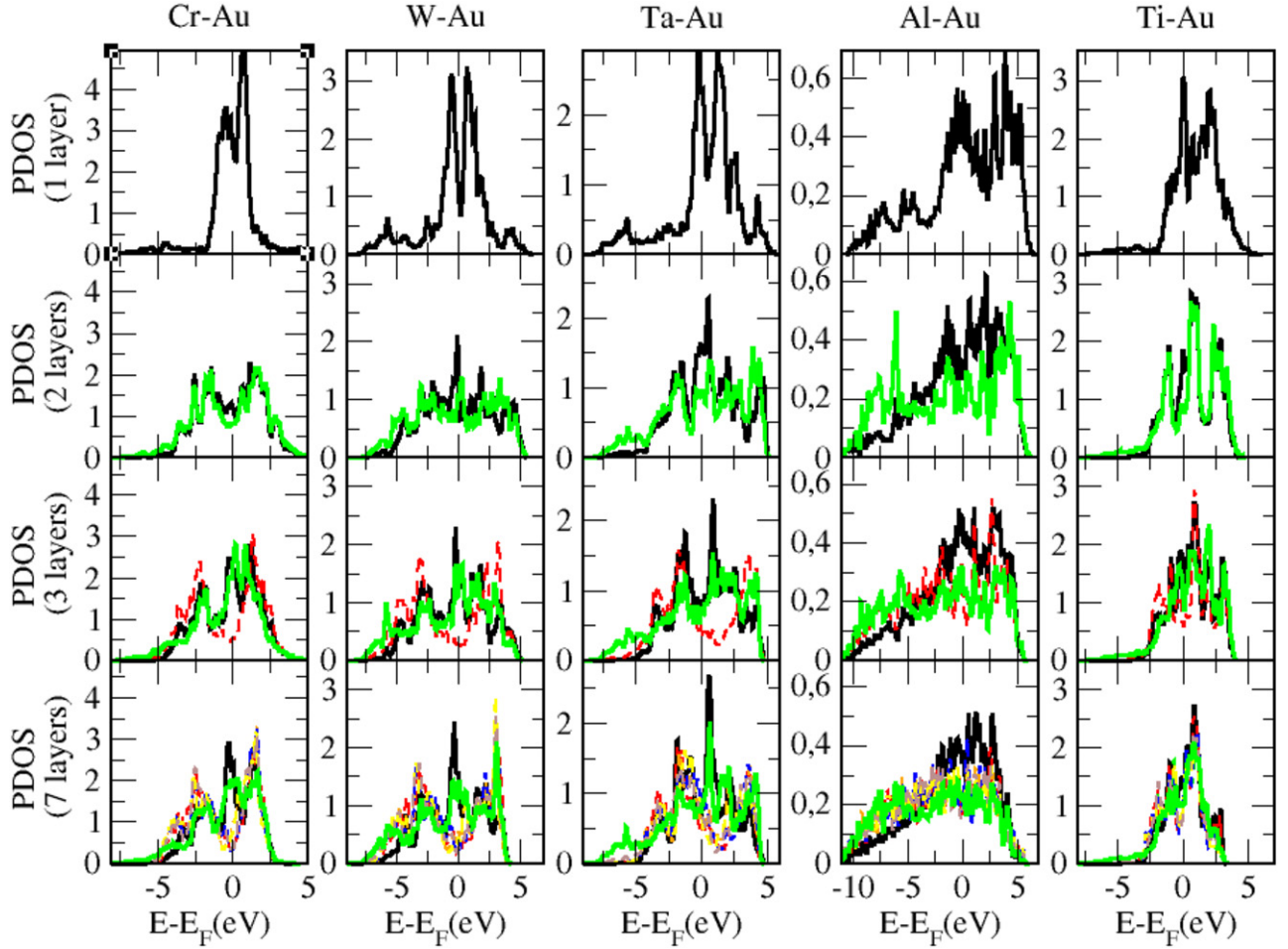


Figure 4. Projected density of states on the d band in each atom inside the adlayer. In each panel, the black curve refers to the outermost atom (in contact with vacuum), the green curve indicates the IL-M atom (in contact with gold), and the red curve refers to the atom closer to the outermost one (which is the middle one in the case of the three-atom thickness.)

what observed in the gold counterpart. Indeed, in all three cases, the trend is approximately reversed with respect to that of the corresponding work of separation. We also noticed that, for these three bcc metals, the total charge transfer was found to be higher for the one-layer case than for the others (see table 1 in the SI for total charge-transfer values). For these three fcc–bcc interfaces, overall, these results seem to indicate that the expected charge transfer from bcc to fcc induces the formation of a higher dipole moment at the interface in the one-layer case as compared to the others, which thus requires more energy to re-establish the initial situation, thus resulting into higher work of separation. These conclusions clearly do not apply, however, to Al and Ti. In the case of Ti, although the work of separation follows the same pattern as for the bcc metals, the highest charge transfer to Au was found for the two-layer case rather than for one-layer case (which is also reflected in the charge of the IL-Au atom). For Al, we did find higher charge transfer for the one-layer case, but this was not reflected in a higher work of separation. Interestingly, the trend of the work-of-separation of the Au–Al interface reproduces, instead, that of the total density of states at the Fermi level, which is however not the case for the other systems (see supporting information). This could

suggest a more quantum (exchange–correlation) driven, rather than electrostatics-driven, adhesion at the Al–Au interface, potentially.

For the three bcc metals, the work of separation follows the order $\text{Au–Ta} > \text{Au–W} > \text{Au–Cr}$ for all numbers of adlayers. This trend is similar to that observed for the bulky interfaces analysed in reference [24] with the same elements. It also follows the experimental trend observed in reference [22]. As mentioned above, the Au–Ti interface appears to be less stable than all the others, which contradicts the aforementioned experiments. We ascribe this difference to the fact that those experiments all used Au crystals in the same orientation Au (111), whereas, in our calculations, we used Au (100) in all cases but for Ti (0001), for which the Au (111) was instead used. However, one also has to bear in mind that the layers considered here are much thinner than those employed in that work. We point out that, in reference [21] it was claimed that, for stability, Cr is better than Ti, opposite to what stated in reference [22].

We now turn to analyse the projected density of states (PDOS) on the d band of all atoms inside the adlayer for all five interfaces and in all four adlayer number cases considered (figure 4). A comparison of the PDOS on the IL-M atom

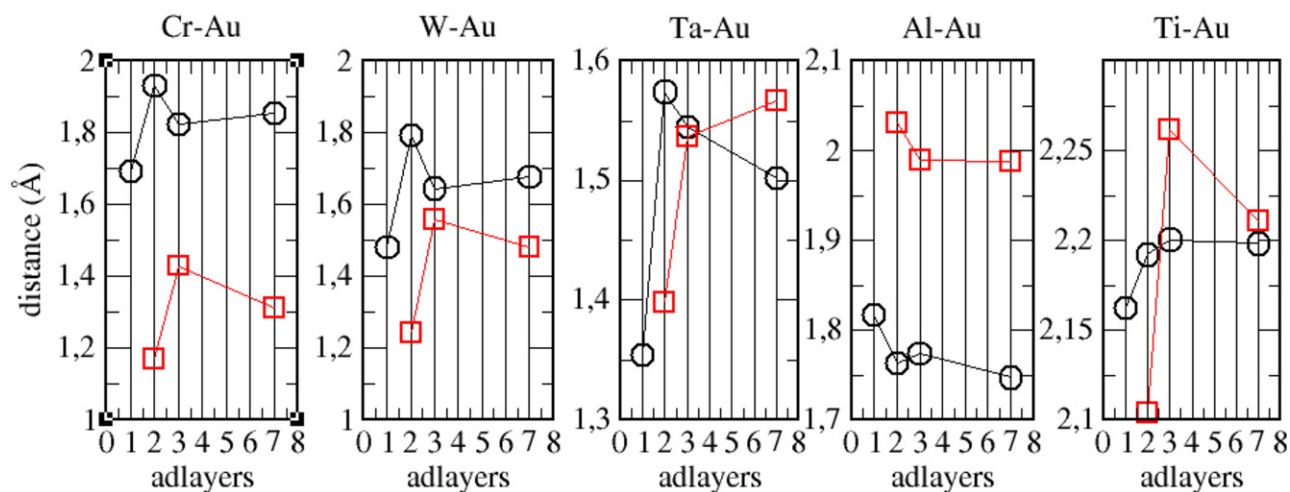


Figure 5. Upper row: distance between the IL-Au atom and the IL-M atom of the adlayer (black circle), and distance between the IL-M atom and the atom immediately next to it within the adlayer (red squares).

in the adlayer and on the IL-Au atom across the four layer-combination cases for each system is shown in the supporting information. We focus on this angular momentum because it is known to play a key role in binding for transition metals [38, 39]. In the case of Al, for which the d band is unoccupied, the p band was instead analysed. In figure 4 it is possible to see that, in the case of one-atom thick adlayer, the height of the peaks is higher than in the corresponding cases with thicker layers, indicating that the adsorbed metal is preserving a more atomic nature in the former case. Conversely, the broader and flatter curves obtained with thicker layers show more bulk traits. In the case of two-atom layers, the curves of the two atoms inside the adlayer are quite similar to each other for all interfaces (except for Au–Al). With three-atom layers, we observe that the IL-M (in contact with gold, green curve) and outermost (in contact with vacuum, black curve) atoms inside the adlayer have very similar electronic structure, whereas the middle one (red curve) is different, especially at the Fermi energy. This detail prompted us to analyse the ion–ion distances between atoms across the layers.

In figure 5, we report the out-of-plane components of the distances between the IL-Au atom and the IL-M atom of the adlayer (black circles). We also show the out-of-plane components of the distances, within the adlayer, between the same IL-M atom and the second atom, i.e., the one immediately next to it (red squares). In the three bcc cases, the two-layer-thickness case presents a shorter distance between the two layers, as well as a larger distance from the gold surface as compared to the other cases. This indicates that, when only 2 adlayers are present, they dimerize. They thus lie at larger distance from Au, leading to a smaller work of separation. Moreover, this is reflected into their very similar electronic structure, as observed in figure 4 (note that a different combination of metals, in which the interface interaction is stronger than the interlayer interaction within the adlayer material, might give rise to a different behaviour). In the case of three-atom films instead, the atom in the middle shows very different electronic structure from the other two, as already mentioned above.

Overall, we observe that the distances between the IL-Au and the IL-M are approximately (qualitatively) inversely proportional to the work of separation (see the supporting information for the complete data for all numbers of Ta layers). It is also worth noting that the trend displayed by the work of separation is also affected by the relative coordination of each layer. For instance, the short distance observed between the outermost layer and the adjacent layer (discussed above for the one- and two-layer case) can be ascribed to the low coordination of the former, which leads to strengthening the bond between those two layers. Indeed, in the case of the Au–Ta interface, such a distance is always found to be the shortest for all numbers of Ta layers (see supporting information). The behaviour observed for the Au–Ta interface, however, does not apply to Au–Al. In this case, the trend shown by the geometrical distances is strikingly different from the bcc cases in that the distances between the IL-Au and IL-M atoms (black circle) are smaller than the inter-layer (red squares) distances, as opposed to the cases described before. Consequently, the two PDOS curves of figure 4 for the two-layer case are no longer similar to each other, as they are in the bcc cases. This is because the IL-M layer is now closer to the gold surface than to the adjacent adlayer, it is more affected by the binding to gold, and no dimerisation takes place. For Au–Al, the largest distance from gold is obtained for the one-layer case, which is also reflected in the smaller work of separation shown by figure 3.

Referring finally to the other non-bcc case, Au–Ti, the smallest distance from gold is obtained for the one-layer thickness, and this also corresponds to the largest work of separation observed in this system for this number of layers. For the two-layer case, the distance between the two adlayers is smaller than the corresponding distance from gold; this is consistent with the similarity of the two corresponding PDOS curves in figure 3, similarly to what observed for the bcc metals. We also observe that the distance from gold is, in all cases, higher than that obtained with other metals. This explains the lower values of work of separation obtained for Au–Ti as compared to the bcc cases, despite the higher charge transfer (i.e., formation of

a higher dipole at the interface). The fact that smaller distances from gold correspond to higher work of separation is further supported by the fact that, for the three bcc metals and for all number of adlayers, the distance between the IL-Au and IL-M atoms follows the order $\text{Cr-Au} < \text{W-Au} < \text{Ta-Au}$, which is the exact opposite of that observed in figure 3 for the work of separation ($\text{Au-Ta} > \text{Au-W} > \text{Au-Cr}$).

Before we conclude, we remind the reader that these calculations were limited to a minimal unit cell (containing one atom in the xy plane, and very long in the z direction). This is consistent with the goal of focusing on differences deriving from differences in the adlayer metal species only, which as we have seen are sufficiently complex to analyse without the addition disorder effects, their experimental relevance notwithstanding. Thus, effects originating from diffusion, mismatch, alloy formation and oxygen absorption [1, 21, 40] were not taken into account. It remains to be seen how such effects would alter our findings. For instance, different mismatches across the interface may lead to non-uniform Au-adlayer distances and this could be in turn reflected into different interlayer distances within the adlayer. This would most likely affect the work of separation. Larger unit cells could, in future work, also be investigated in order to minimize the strain at the interface deriving from imposing unit-cell sizes obtained from bulky interfaces and thus, perhaps, to obtain more energetically-favoured, reorganised interfaces. More demanding calculations will be needed, therefore, in future, in order to clarify all these issues. Due to the need to incorporate a sufficient vacuum region for converged results, first-principles slab calculations within density-functional theory are particularly challenging using plane-wave bases, and hence a strictly localised-orbital basis may provide a more promising means to this end. The effect of employing more refined exchange–correlation functionals could also be explored. Finally, it is worth noting that our calculations were based on low-index crystal orientations that ensure optimal matching at the interface (for instance, for $\text{bcc}(100)/\text{Au}(100)$). Although we envisage that other orientations with a less optimal match, such as $\text{bcc}(100)/\text{Au}(111)$, would give rise to more unstable interfaces, ad-hoc calculations could be carried out in future (with larger unit cells) to explore the thickness dependence of the work of separation for these kinds of systems and learn how it compares with the behaviour shown by the structures analysed in this work.

3. Conclusions

We have studied interfaces consisting of thin atomic layers of five different metals (Cr, W, Ta, Al and Ti) on Au. The computed work of separation as a function of thickness of the adlayer showed oscillations which are higher for a low number of layers and which gradually decrease with increasing thickness. For the bcc metals (Cr, W and Ta) and for Ti, we found that one layer leads to the highest work of separation. It was also found that 2 layers lead to a minimum work of separation, which was explained with dimerization of the two adlayers. The Au–Al interface showed a different trend, which probably stems from its p character and the different crystal structure

(fcc), although the oscillations observed in this case were one order of magnitude lower than in the other systems. For all cases, the distance between innermost adlayer and the gold was found to follow approximately the opposite trend of the work of separation. Within the bcc set, the work of separation was furthermore found to follow approximately the trend of the charge transfer taking place from the bcc to fcc metal.

4. Methods

We carried out density functional theory (DFT) calculations by using the PWscf code of the Quantum ESPRESSO distribution [41], which is based on plane-wave bases. The LDA exchange–correlation functional was adopted, with a kinetic energy cutoff for wave-functions of 50 Ry and of 400 Ry for the charge density and potential. We chose this functional because it has been found to yield better agreement with experiments for surface energies as compared to GGA [42]. It has also proven to provide a very good description, given its relative computational cost-effectiveness, of structural and energetic properties of solids [43]. Moreover, trends observed in interface energies we previously evaluated by this method [24] were later confirmed by recent experiments [22]. For the Brillouin-zone integration, we used a Monkhorst–Pack [44] set with a $16 \times 16 \times 1$ k -point grid. A Fermi–Dirac smearing with a broadening of 0.0038 Ryd (≈ 600 K) was adopted. Ultrasoft pseudopotentials USPPs [45] were used for all elements. The size of the unit cell along the z (interface) direction was from 70 to 80 Å in all calculations. As for the in-plane (xy) size of the cell, it was determined by preliminary calculations on bulky interfaces of the same metals (such as those considered in reference [24], in which optimization of the cell size was allowed in all three Cartesian coordinates. The strain induced at the interface was reported in the supporting information of the same article. Each layer contained one atom. The orientation of Au was (100) for interfaces with Cr(100), W(100), Ta(100) and Al(100), and (111) for the interface with Ti(0001). For the interface with Cr, W and Ta, the (100) faces of the two metals were rotated in-plane by 45 degrees with respect to each other so as to provide an optimal match between the bcc lattice constant a_{bcc} and half a diagonal of the fcc face ($a_{\text{fcc}}/\sqrt{2}$, where a_{fcc} is the fcc lattice constant) [46]. For the interface with Ti (0001), the (111) orientation of Au was chosen so as to take advantage of the hexagonal symmetry of both surfaces. Specifically, the a parameter of Ti approximately matches with the interatomic Au–Au distance within the (111) plane.

Acknowledgments

This publication has emanated from research supported in part by a grant from Science Foundation Ireland under Grant numbers [12/RC/2278_P2], and is co-funded under the European Regional Development Fund under the AMBER award. For the purpose of Open Access, the author has applied a CC BY public copyright licence to any Author Accepted Manuscript version arising from

this submission. All calculations were performed on the Boyle cluster maintained by the Trinity Centre for High Performance Computing and funded through grants from the European Research Council and Science Foundation Ireland. DDO'R acknowledges John F Donegan, William M Abbott, and Christopher P Murray for discussions. LAZ thanks the Universidad Autónoma de Madrid and the Comunidad de Madrid (Grant No. SI3/PJI/2021-00191) and the Spanish MINECO 'María de Maeztu' Programme for Units of Excellence in R & D (Grant No. CEX2018-000805-M).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

Linda A Zotti  <https://orcid.org/0000-0002-5292-6759>

David D O'Regan  <https://orcid.org/0000-0002-7802-0322>

References

- [1] Wang Y-S, Zhou X, Tomko J A, Giri A, Hopkins P E and Prezhdov O V 2019 *J. Phys. Chem. C* **123** 22842–50
- [2] Palotás K, Bakó I and Bugyi L 2016 *Appl. Surf. Sci.* **389** 1094–103
- [3] Abbott W M *et al* 2019 *ACS Appl. Mater. Interfaces* **11** 7607–14
- [4] Hung A, Yarovsky I, Muscat J, Russo S, Snook I and Watts R O 2002 *Surf. Sci.* **501** 261–9
- [5] Jiang D, Long J, Cai M, Lin Y, Fan P, Zhang H and Zhong M 2017 *Mater. Des.* **114** 185–93
- [6] Hoseini Athar M M and Tolaminejad B 2015 *Mater. Des.* **86** 516–25
- [7] Han T-Z, Dong G-C, Shen Q-T, Zhang Y-F, Jia J-F and Xue Q-K 2006 *Appl. Phys. Lett.* **89** 183109
- [8] Emadinia O, Ramalho A M, de Oliveira I V, Taber G A and Reis A 2020 *Metals* **10** 997
- [9] Lü X *et al* 2019 *Sci. Bull.* **64** 1567–72
- [10] Saikia U, Sahariah M B, González C and Pandey R 2018 *Sci. Rep.* **8** 1–12
- [11] James R A, Stapleton A J, Hughes A, Charrault E, Zuber K, Switalska E, Evans D, Murphy P and Llusca M 2018 *Adv. Eng. Mater.* **20** 1800106
- [12] Feldbauer G, Wolloch M, Bedolla P O, Mohn P, Redinger J and Vernes A 2015 *Phys. Rev. B* **91** 165413
- [13] Linghu Y, Wu X, Wang R, Li W and Liu Q 2016 *Crystals* **6** 32
- [14] Park N-Y, Choi J-H, Cha P-R, Jung W-S, Chung S-H and Lee S-C 2012 *J. Phys. Chem. C* **117** 187–93
- [15] González C and Iglesias R 2016 *Mater. Des.* **91** 171–9
- [16] Dang D Y, Shi L Y, Fan J L and Gong H R 2015 *Surf. Coat. Technol.* **276** 602–5
- [17] Ren Q Q, Fan J L and Gong H R 2015 *Mater. Lett.* **145** 205–8
- [18] Anadón A, Guerrero R, Jover-Galtier J, Gudín A, Díez J, Ollerós-Rodríguez P, Miranda R, Camarero J and Perna P 2020 *arXiv:2003.07677*
- [19] Flores G G B, Kovalev A A, van Schilfgaarde M and Belashchenko K D 2020 *Phys. Rev. B* **101** 224405
- [20] Leandro L, Malureanu R, Rozlosnik N and Lavrinenko A 2015 *ACS Appl. Mater. Interfaces* **7** 5797–802
- [21] Todeschini M, Bastos da Silva Fanta A, Jensen F, Wagner J B and Han A 2017 *ACS Appl. Mater. Interfaces* **9** 37374–85
- [22] Abbott W M *et al* 2020 *ACS Appl. Mater. Interfaces* **12** 13503–9
- [23] Han Y, Evans J W and Liu D-J 2008 *Surf. Sci.* **602** 2532–40
- [24] Zotti L A, Sanvito S and O'Regan D D 2018 *Mater. Des.* **142** 158–65
- [25] Hu J, Xie M, Chen Y, Fang J and Yang Y 2019 *Comput. Mater. Sci.* **169** 109133
- [26] Benedek R, Seidman D N and Woodward C 2002 *J. Phys.: Condens. Matter* **14** 2877
- [27] Lu S, Hu Q-M, Punkkinen M P J, Johansson B and Vitos L 2013 *Phys. Rev. B* **87** 224104
- [28] Chen M, Qin W, Wang Y and Jiang Y 2019 *Surf. Coat. Technol.* **378** 125082
- [29] Khalid M Z, Friis J, Ninive P H, Marthinsen K and Strandlie A 2021 *Comput. Mater. Sci.* **187** 110058
- [30] Bakulin A V, Kulkov S S, Kulkova S E, Hocker S and Schmauder S 2020 *Metals* **10** 1298
- [31] Jeong I S, Ahn E G and Lee J H 2020 *Phys. Rev. B* **102** 075441
- [32] Erramilli S, Neumann T V, Chester D, Dickey M D, Brown A C and Genzer J 2020 *RSC Adv.* **10** 11348–56
- [33] Forti M, Alonso P, Gargano P and Rubiolo G 2015 *Proc. Mater. Sci.* **8** 1066–72
- [34] Fiolhais C, Almeida L M and Henriques C 2003 *Prog. Surf. Sci.* **74** 209–17
- [35] Han Y and Liu D-J 2009 *Phys. Rev. B* **80** 155404
- [36] Li W, Huang L, Pala R G S, Lu G-H, Liu F, Evans J W and Han Y 2017 *Phys. Rev. B* **96** 205409
- [37] Ming W, Blair S and Liu F 2014 *J. Phys.: Condens. Matter* **26** 505302
- [38] Tang W and Henkelman G 2009 *J. Chem. Phys.* **130** 194504
- [39] Nørskov J K, Abild-Pedersen F, Studt F and Bligaard T 2011 *Proc. Natl. Acad. Sci. USA* **108** 937–43
- [40] Martinez W E, Gregori G and Mates T 2010 *Thin Solid Films* **518** 2585–91
- [41] Giannozzi P *et al* 2009 *J. Phys.: Condens. Matter* **21** 395502
- [42] Singh-Miller N E and Marzari N 2009 *Phys. Rev. B* **80** 235407
- [43] Pérez R and Gumbsch P 2000 *Acta Mater.* **48** 4517–30
- [44] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [45] Garrity K F, Bennett J W, Rabe K M and Vanderbilt D 2019 GBRV high-throughput pseudopotentials <https://physics.rutgers.edu/gbrv/>
- [46] Haney P M, Waldron D, Duine R A, Núñez A S, Guo H and MacDonald A H 2007 *Phys. Rev. B* **75** 174428