

Comparative study of Ag, Au, Pd, and Pt adsorption on Mo and Ta (112) surfaces

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The structural, energetic, and electronic properties of low-coverage phases of Ag, Au, Pd, and Pt atoms adsorbed on the (112) surface of Mo and Ta are investigated from first principles. On Mo(112) the binding energy of adatoms increases with coverage (for dimers, linear trimers, and infinite chains) which means the prevalence of attractive interactions between adatoms in the same trough and their clustering. This is at variance from the behavior on the Ta surface where the binding per adatom in dimers or trimers is decreasing or not altered compared to a single atom adsorption. Consequently, on Mo(112) adatom chains form in the furrows as experimentally observed, whereas on Ta(112) the adatoms are more likely to form a scattered, random pattern. Pd and Pt adsorbates are predicted to mix and alloy with Ta(112) atoms.

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I. INTRODUCTION

Adatom behavior on metal surfaces is a fundamental element for understanding of many surface phenomena such as, e.g., nucleation and growth, nanostructuring, surface alloying, etc.¹ An overlayer of metallic atoms can drastically change both the electronic and chemical properties of the metal surface. This was already recognized in the early days of the electronics industry and contributed greatly to the development of surface science. The (112) surface of bcc metals consists of troughs separated by ridges. Such a structure of the substrate may be considered as a template for the formation of the ordered adatom chains that follow the furrows. However, the experimental studies of submonolayer adsorption of metallic atoms on the bcc (112) surface of transition metals discovered a wider diversity of ordered adatom structures. It was found that the *sp*-bonded alkali- and alkaline-earth-metal atoms, adsorbed on Mo and W(112) surface, can form commensurate chain structures of long periodicity, aligned normal to the furrows.² These structures, which are to a large extent dictated by the underlying surface, provide evidence for a strong anisotropy of adatom lateral interactions and were recently confirmed by our first-principles calculations.³ In contrast, transition metal adatoms, for example Au atoms on W(112) and Pd on Mo(112), form long atomic chains following the close-packed [111] directions.^{4,5} Palladium atoms were observed to form similar pseudomorphic adsorbate rows on W(112).⁶ The occupied troughs are separated by three or two unoccupied ones, respectively, for Au and Pd, while the Pt-atom chains are distributed at random. Recently, investigations of the properties of linear chains of Au and Pt and their coupling to metallic substrate have gained considerable interest in the context of fabrication and characterization of nanowires.⁷

Here we examine the properties of low-coverage structures of four transition fcc metals adsorbed on Mo(112) and Ta(112). Among the transition metals, Ag and Au have approximately the same nearest neighbor distance as tantalum, while in Pd and Pt, this distance is close to that of molybdenum. Both Mo and Ta crystallize in the bcc structure and their lattice parameters⁸ differ only by 5%. This suggests that adsorption of Ag, Au, Pd, and Pt on the Mo and Ta surfaces should not create significant strain. Molybdenum is a 4*d*

metal while tantalum is a 5*d* metal. Pd and Ag are neighbors in the periodic table and differ in their electronic structure only for the presence of one electron in a 5*s* shell. Au differs from its neighbor Pt with its closed 5*d* outer shell configuration by a 6*s* valence electron. According to field-ion microscopy (FIM) observations, only adsorbate metals with more than half-filled *d*-electron shells form long chain structures on densely packed substrates.⁹ Though this condition is satisfied for the adsorbates considered here, it is interesting to study the difference between adsorption of a noble metal, with completely filled outer *d* band, and that of a transition metal, interacting with different transition metal substrates. Most of these structures were confirmed to be also formed on large area surfaces by low-energy electron diffraction (LEED).¹⁰ Our focus is on the possibility of formation of ordered structures of the noble and transition metal adatoms corresponding to coverages below one monolayer (ML) at two atomically similar transition metal surfaces. To our knowledge these systems have not been studied from first principles. Some of the adatoms and substrates (e.g., Pd-Mo) can form alloys, which adds extra complexity to these systems.

The paper is organized as follows. Section II outlines the methodology of the calculations. In Sec. III we analyze and discuss our results, and Sec. IV provides a brief summary.

II. METHOD

The calculations employ density-functional theory in the generalized gradient approximation for the exchange-correlation energy functional,¹¹ as implemented in the Vienna *ab initio* simulation package (VASP).¹² The electron interaction with the ionic cores is represented by the projector augmented-wave potentials.^{13,14} A plane-wave basis with kinetic energy cutoff of 250 eV is applied. The structural parameters of the bcc Mo and Ta (the lattice parameter and the bulk modulus) as well as the bare (112) surface properties (the relaxations of atomic planes) were determined by us previously^{3,15} in good agreement with the experimental data. Also electronic-property-related quantities such as surface energy and work function of the clean (112) surfaces of Mo and Ta are well reproduced. The bcc(112) surface is modeled by periodically repeated slabs consisting of seven atomic

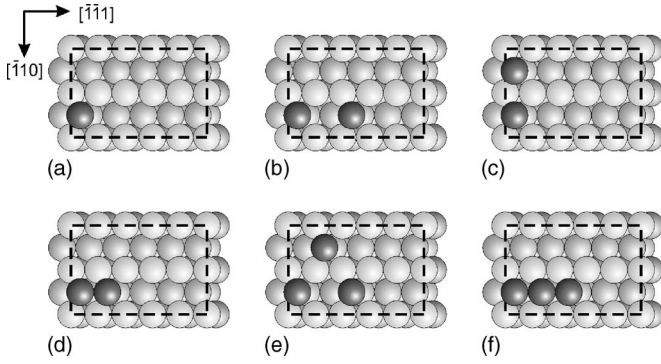


FIG. 1. Geometry of the original adatom structures on the bcc(112) surface showing the 5×2 unit cell applied in the calculations. The adatom sites in atomic furrows correspond to positions occupied by substrate atoms in the bulk.

layers separated by eight equivalent layers of vacuum. A $4 \times 6 \times 1$ k -point mesh generated by the Monkhorst-Pack scheme¹⁶ was applied to sample the Brillouin zone, with the 0.2 eV smearing¹⁷ of the occupied states. The atoms were adsorbed on one side of the slab (a dipole correction^{18,19} was applied to compensate for an artificial electric field) in the bulk bcc(112) positions, i.e., the ones that would be occupied by the atoms of an additional substrate layer. All adatoms and the atoms of the four topmost substrate layers were free to optimize their positions, until the Hellmann-Feynman forces converged to less than 0.02 eV/Å per atom.

The binding energy E_b of an adatom with respect to the energy of a free adsorbate atom, E_{ad} , is calculated as follows:

$$E_b = -\frac{1}{N}[E_{ad/M(112)} - E_{M(112)} - NE_{ad}], \quad (1)$$

where $E_{Ad/M(112)}$ is the total energy of the relaxed slab with N adsorbate atoms per unit cell, and $E_{M(112)}$ is the energy of the relaxed substrate slab. All values are calculated with the same supercell size, cutoff energy, and k -point mesh. The initial geometries of the structures considered for coverages 0.1, 0.2, and 0.3 ML are presented in Fig. 1. For Au and Pt on Mo(112) infinite chains (0.5 ML coverage) were also considered, corresponding to every second trough being filled with adatoms.

The calculated binding energies for the same coverage of Ag, Au, Pd, Pt atoms, in unit cells of different sizes, and the same density of k points (for example, a single adatom in the 5×1 and two evenly spaced adatoms in the neighboring troughs of the 5×2 cell [Fig. 1(c)], with $4 \times 12 \times 1$ and $4 \times 6 \times 1$ k -point meshes, respectively) are converged to within 1 meV. The accuracy in the determination of the relative energies presented here (the same unit cell) can be estimated as being well within ± 5 meV.

III. RESULTS AND DISCUSSION

A. Surface geometry

Metal atom adsorbates have a stabilizing effect on the substrate surface. This is manifested in derelaxation of the

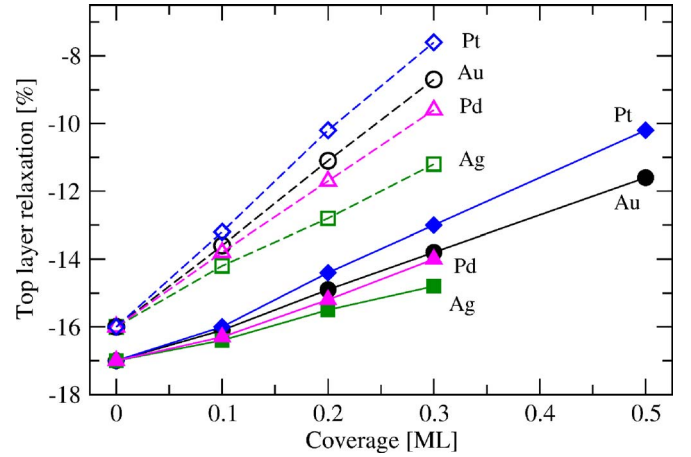


FIG. 2. (Color online) Change in the vertical relaxation of interlayer distance of the outermost layers of (112) surface of Mo (full symbols) and Ta (open symbols) upon adsorption of Ag, Au, Pd, and Pt.

topmost atomic planes (Fig. 2). A contraction of the average interlayer distance between the topmost layers of the Mo and Ta substrates decreases with increasing adatom coverage Θ . It varies from -17% for clean Mo(112) down to -10% for 0.5 ML of Pt. Similarly on Ta(112) it drops from -16% to -8% for 0.3 ML of Pt. The derelaxation effect increases from Ag via Pd and Au to Pt atoms. The relaxation of deeper layers also changes with adsorption. The results for a coverage of 0.2 ML are shown in Table I. As seen in this table, the adsorbate covered surfaces of the two substrates show simi-

TABLE I. Change in the average geometry of the four outer layers of Mo(112) and Ta(112) upon adsorption of 0.2 ML of Ag, Au, Pd, and Pt atoms. For the Mo surface only the changes due to (most stable) dimers occupying the same-trough sites are presented. For the Ta surface (b) and (c) refer to Fig. 1. Δd_{ij} are the vertical relaxations of interlayer distance (in % of the bulk interlayer spacing).

System	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}
Mo(112)				
Clean	-17.0	-1.00	2.92	-0.28
Ag	-15.5	-0.98	2.49	-0.41
Au	-14.9	-1.20	2.43	-0.34
Pd	-15.2	-1.28	3.03	-0.53
Pt	-14.4	-1.40	2.94	-0.66
Ta(112)				
Clean	-16.0	1.71	-0.47	-0.84
Ag	-12.8	-0.12	0.88	-1.17
Au	-11.1	-1.38	1.55	-1.36
Pd	-11.7	-0.41	0.91	-1.10
Pd(b)	-11.6	-0.26	0.74	-1.03
Pd(c)	-12.2	-0.27	0.76	-0.90
Pt	-10.2	-1.01	1.18	-1.19
Pd(b)	-10.3	-0.84	1.04	-1.12
Pd(c)	-11.3	-0.42	0.83	-1.03

TABLE II. Binding energy (in eV) per atom adsorbed in volume sites of the 5×2 surface cell of the (112) surface of Mo and Ta. The labeling of patterns refers to panels in Fig. 1. The data for the most stable structures at a given coverage are printed in bold.

Coverage (ML)	Pattern	Mo(112)				Ta(112)			
		Ag	Au	Pd	Pt	Ag	Au	Pd	Pt
1/10	a	2.870	3.831	4.508	6.528	3.113	4.289	5.147	7.489
2/10	b	2.862	3.822	4.505	6.524	3.079	4.252	5.116	7.445
	c	2.894	3.820	4.470	6.450	3.024	4.185	5.110	7.446
	d	2.907	3.846	4.567	6.587	3.051	4.189	5.110	7.404
	e	2.876	3.811	4.472	6.460	3.122	4.292	5.147	7.486
3/10	f	2.927	3.865	4.617	6.669	3.043	4.173	5.120	7.400
	∞		3.920		6.852				

lar relaxation patterns, namely, $--+-$, where minus and plus signs denote contraction and expansion, respectively. The relaxations of deeper layers are much smaller compared to the topmost layer (Fig. 2) and do not exceed 3%. The vertical shifts of the particular atoms of the various Mo layers (surface buckling) relative to the center-of-mass position of the layers, are rather small and, in most cases, do not exceed 0.04 Å. On the Ta(112) surface these shifts are larger than those on Mo(112). The largest shifts of substrate atoms are observed for infinitely long Au, and Pt, chains (0.5 ML). In this case every second furrow is filled completely with adatoms which push the underlying Mo atoms. As a consequence the vertical positions of Mo atoms of the second layer below the adsorbate, and those in an empty furrow differ by 0.12 Å and 0.19 Å, for Au and Pt chains, respectively. The Mo atoms of the topmost and the third layer remain unbuckled.

The atomic planes of the clean bcc(112) surface shift laterally as a whole in the $[\bar{1}\bar{1}1]$ direction by ~ 0.1 Å and increase the coordination of atoms with respect to the neighboring layers.¹⁵ A more detailed analysis of the bonding geometry shows quite a complicated rearrangement of the atomic positions in the (three) topmost layers. The typical change in geometry of the surface caused by a single adatom is as follows. The adatom shifts in the $[\bar{1}\bar{1}1]$ direction and takes a more coordinated position, closer to the half-distance between atoms of the topmost substrate layer. This shift is larger for Ag and Au (≈ 0.23 – 0.26 Å) than for Pd and Pt (≈ 0.06 – 0.04 Å). The position of the substrate atom, most directly below the adatom, is lowered by 0.04 Å for Ag and up to 0.08 Å (Pt), with respect to the average (center-of-mass) position of atoms in the relaxed second top atomic plane. The substrate atoms of the topmost $[\bar{1}\bar{1}1]$ rows next to the adatom are displaced in the $[\bar{1}10]$ direction by about 0.02 Å (Ag) up to 0.05 Å (Pt). Because the atomic radii of Ag, Au, Pd, Pt adsorbates, and of Mo and Ta substrates, do not differ significantly ($\approx 5\%$), the longer adsorbate chains form nearly pseudomorphic rows.

B. Bonding properties

1. Binding energy

All considered metals bind strongly to the substrate (Table II). On both substrates the binding increases in the order Ag,

Au, Pd, Pt, and is more than doubled for Pt compared to Ag. All adatoms bind stronger (by 10–15 %) to Ta than to Mo. Judging by the differences in the binding energies of monomers, dimers, and trimers, the tendency of the adatoms on Mo(112) to order in a chain is increasing in the order Au, Ag, Pd, and Pt. The energy difference between various structures on Mo(112) varies between 50 meV (Au), and 200 meV for Pt, for $0.1 \leq \Theta \leq 0.3$ ML. On Ta(112) the trend is reversed: the difference is largest for Au (120 meV) and smallest for Pd (40 meV). These values compare well with the differences in the binding of Li and Sr (without d electrons in the outer valence shell) on Mo(112), which we reported previously.³ Direct measurements of the binding energy of metal adsorbates are complicated and scarce. Experimental data of adsorption energies of single atoms on Mo(112) and Ta(112) are not available. Usually the information on binding energies is extracted from field or thermal desorption experiments, and surface diffusion data. It should thus be noted that the experimental binding energy may depend on the method used.¹

Our results for Ag and Au adsorption on Mo(112) can be compared only with experimental desorption energies (at the zero-coverage limit) for Ag (3.7 eV) and Au (4.2–4.3 eV) on the W(112) surface⁴ whose properties are quite close to those of Mo(112). The values calculated for Mo(112) compare quite well with those numbers, the difference between the calculated numbers being, however, twice as large, to give ~ 1 eV (Table II). For Mo(110) the binding energy of an isolated Au atom determined²⁰ by the temperature-programmed desorption amounts to 3.70 eV.

On Mo(112) formation of atomic chains (clustering) along the troughs is favored. For the most compact chain structures the binding energy increases with coverage (Table II). The strongest binding is found for the adatoms in the three-atom, and in infinite, chains. The configuration with the single atom has an adsorption energy 0.09 eV (Au), and 0.32 eV (Pt) smaller than in the respective infinite chain. The former number compares well with the energy of sublimation (0.13 eV/atom) of two-dimensional Au adsorbate gas on W(112).²¹ It shows that the attractive interactions between adatoms within the same trough increase the binding energy with increasing clustering. The formation of the adatom chains agrees with the experimental observations of stable

Pd chain structures on Mo(112).⁵ Au chains were observed on the W(112) surface,⁴ where the formation of short rows of Ag atoms also was not excluded. The one-dimensional Pt chains along the $\langle 111 \rangle$ direction on W(110) were observed by LEED at every third substrate row.²²

For Ta(112) linear chains are distinctly unfavored (Table II) and a random distribution of adatoms is more likely. This indicates a weaker interaction with the substrate and a predominance of repulsive interactions along the furrows. The proximity of the second atom in a dimer, or in a trimer, decreases the binding energy per atom by some 30–110 meV, which is much larger than the numerical uncertainty of our calculations.

The preference of a more scattered adatoms distribution on Ta(112) agrees with the experimental findings for large area surfaces^{23,24} where no chains of Au, Pd, or Pt were observed. On the other hand, chain structures were reported for Ag.²³ FIM measurements showed that Pd atoms also form chains oriented in the close-packed direction on Ta(110).²⁵ However, a photoemission study²⁶ showed that the bonding of single Pt or Pd atoms on Ta(110) is stronger than of an atom in the monolayer, thus supporting our findings that adsorbate chains on this surface are unlikely.

There are no experimental data on single atom adsorption binding energies on Ta(112) for comparison with our results. However, reasonable estimates of this quantity can be provided by using data for the activation energy for surface diffusion. This energy is typically about 10% of the binding energy.²⁵ The energy for Pd diffusion on Ta(110), extracted from the FIM experiments, amounts to 0.49 eV.²⁵ Assuming that the approximate ratio of the desorption energies,⁴ observed for Au and Ag on tungsten surfaces, $E_{\text{des}}(110)/E_{\text{des}}(112) \approx 0.8$, holds also for the Pd/Ta system, one obtains 6.1 eV for the binding energy of Pd on Ta(112). This is about 20 % higher than the value given in Table II, but this rough estimate shows that the calculated binding energies for the metal adsorbate/Ta(112) system are quite realistic. It should be noted, however, that the above ratio is not universal. FIM studies of the transition metal (Ta, W, Re, Ir) diffusion on the (110) and (112) tungsten surfaces showed^{27,28} that the $E_{\text{des}}(110)/E_{\text{des}}(112)$ ratio is ≈ 1.6 (Ta)–1.18 (Re). Also, the estimate presented above does not take into account the increased atom rearrangement at Ta(112),¹⁵ which modifies the adsorbate binding. On the other hand, the heat of adsorption, deduced from a photoemission study,²⁶ yielding 0.4 eV/atom for Pd/Ta(110), is greatly underestimated.

2. Bond length

The calculated adsorbate-substrate bond lengths (Table III) do not depend (within 1%) on the substrate, for all considered adsorbates. They are close to, but smaller than, the sum of metallic radii²⁹ for the respective adatom-Mo and adatom-Ta pairs. This demonstrates a substantial metallic contribution to the bond. The bond length increases slightly (~ 0.02 Å) with Ag and Au coverage, and does not change for Pd and Pt on Mo(112). It decreases by a similar amount for all adsorbates in the chainlike structures on Ta(112).

TABLE III. Bond length between a single adsorbate atom and the underlying substrate atom on the Mo and Ta(112).

Surface	Bond length (Å)			
	Ag	Au	Pd	Pt
Mo(112)	2.75	2.70	2.61	2.58
Ta(112)	2.77	2.70	2.59	2.55

The adatom-adatom distance in the chains is similar for Ag and Au, and Pd and Pt dimers on each substrate. On the Mo(112) surface it is 2.91 Å (Ag) and 2.94 Å (Au), and 2.87 Å (Pd) and 2.82 Å (Pt), respectively. These numbers are very close to twice the ionic radius of the atoms.²⁹ On the Ta(112) surface the linear structures are not favored and the adatom-adatom distance in dimers and trimers is increased by ~ 3 –4 %. This on one hand reflects the larger surface lattice constant along the close-packed $[111]$ direction, which dictates the adatom distribution in the sites, while on the other, it indicates a weakening of the attractive interaction along the troughs. For all trimers, independently of the Mo or Ta surface, the adatom-adatom distance is slightly (by 1–3 %) shrunk compared to that in the dimers.

The increase of the binding energy with coverage is, in general, accompanied by a small increase in the vertical distance of the adatoms to the topmost substrate planes. Figure 3 displays the adatom-surface distance for adsorption of a single atom on Mo(112) and Ta(112) versus the empirical covalent radius⁸ of the atoms. The distance is measured with respect to the center of gravity of the topmost, and the sec-

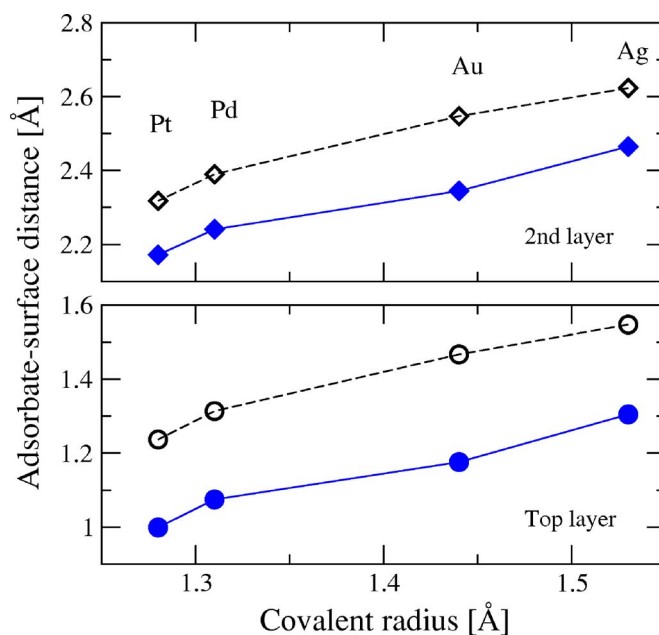


FIG. 3. (Color online) The adatom-surface distance for single atom adsorption versus empirical covalent radius (Ref. 8) of the adatom. Circles represent the distance to the center of gravity of the uppermost layer while diamonds are the distance to the second atomic layer (beneath the adatoms). Filled and open symbols mark the results for Mo(112) and Ta(112) surfaces, respectively.

TABLE IV. Work function change (in meV) for single atoms adsorbed on the (112) surface of Mo and Ta [calculated with respect to work function of the clean metal surface $\Phi_{\text{Mo}(112)}=4.108$ eV, $\Phi_{\text{Ta}(112)}=4.031$ eV]. The labeling of patterns refers to Fig. 1. The data for the most stable structures at given coverage are printed in bold.

Coverage [ML]	Pattern	Mo(112)				Ta(112)			
		Ag	Au	Pd	Pt	Ag	Au	Pd	Pt
1/10	a	9	137	50	129	19	89	38	93
2/10	b	10	251	86	239	45	187	85	206
	c	10	222	78	233	53	188	70	174
	d	61	264	121	285	61	192	104	218
	e	19	342	118	356	74	261	109	253
3/10	f	108	376	177	394	121	302	151	308
	∞		592		563				

ond uppermost layers. As is seen, both quantities correlate linearly. The distance is smallest for the Pt, and largest for Ag atoms. It is seen that all adatoms sit ≈ 0.2 Å deeper in the troughs of Mo(112) than on Ta(112), which is only partly due to the smaller atomic radius (~ 0.1 Å) of Mo relative to Ta. It is worth noting that our results reverse the trend resulting from an approximate tight-binding study of the stability of $5d$ dimers on W(112) and Ta(112) which reported³⁰ the $5d$ monomers and dimers to be ≈ 0.1 Å closer to the tantalum than to the tungsten surface.

3. Work function

In general, the work function change of the substrate upon adsorption depends on the electronegativity of the adsorbed atom. If the adsorbate is more electronegative than the substrate, the work function of the substrate increases. All adatoms considered here are distinctly more electronegative on the Pauling scale than Ta (1.5) and, with the exception of Ag (1.93), also more electronegative than Mo (2.16). For small coverages of all the adsorbates considered here (Table IV) the work function increases up to 0.3–0.4 eV [for 0.3 ML of Pt on Ta(112) and Mo(112), respectively]. At a given coverage this increase is higher for chainlike dimers and trimers along the troughs. This small work function enhancement at low coverages agrees well with the measurements for Ag and Au,²³ and Pd and Pt on the Ta(112) (Ref. 24) and Mo(112) surfaces.⁵ The reported work function increase for Au/W(112) amounts to 0.5 eV at low coverage (≈ 0.4 ML).³¹ Earlier measurements for thin layers of Ag and Au on W(112) have shown³² that Ag, contrary to Au, causes work function lowering with increasing coverage. This suggests that this effect depends on the substrate.

The largest work function increase that is observed for compact chains, is easily understood as resulting from the effect of atomic and electron smoothing of the surface.³³ This means that the work function is rather sensitive to the packing density in the adsorbate layer. On both substrates the work function changes are largest for the Pt and Au adsorption, and smallest for Ag adatoms. This seems to be an electronic, rather than a geometrical effect. The larger the atomic

radius of the adsorbate, the further away from the surface is the atom, but this does not necessarily mean that the induced dipole moment is also larger.

The increase in the work function upon adsorption results in an increased dipole moment that is oriented inward (i.e., with a negative charge on the vacuum side). It reflects the electron transfer from the substrate to a more electronegative adatom. The induced dipole moment per adatom (Fig. 4) is much larger on Ta than on the Mo(112) surface. It decreases with the number of adatoms in the chain, which is usually considered as a consequence of the reduced dipole-dipole interaction due to depolarization. The results presented in Fig. 4 show that the depolarization effect is significant and much larger for the Ta surface. However, one also finds that for the less compact structures, independently of the substrate, the dipole moment is even more reduced than for the

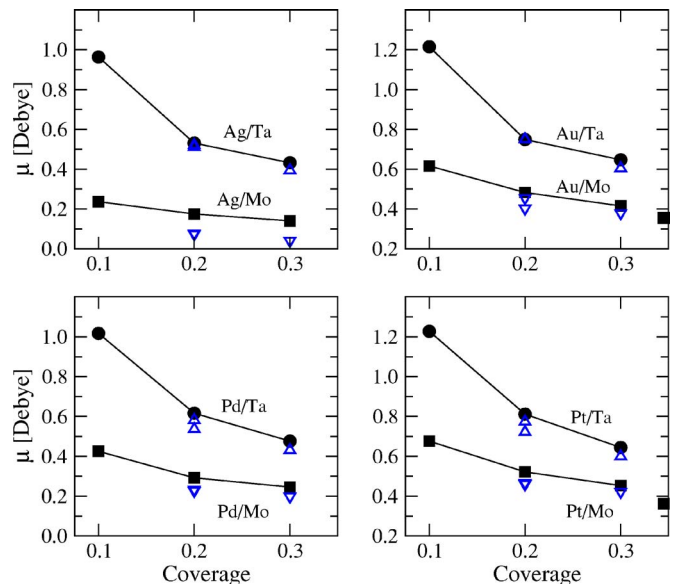


FIG. 4. (Color online) Calculated dipole moments, μ , for various adatom structures on the Mo and Ta(112) surfaces. Filled symbols are for the compact chain structures, while the open triangles represent the sparse structures (see Fig. 1). The full squares to the right represent the results for infinite chains (0.5 ML).

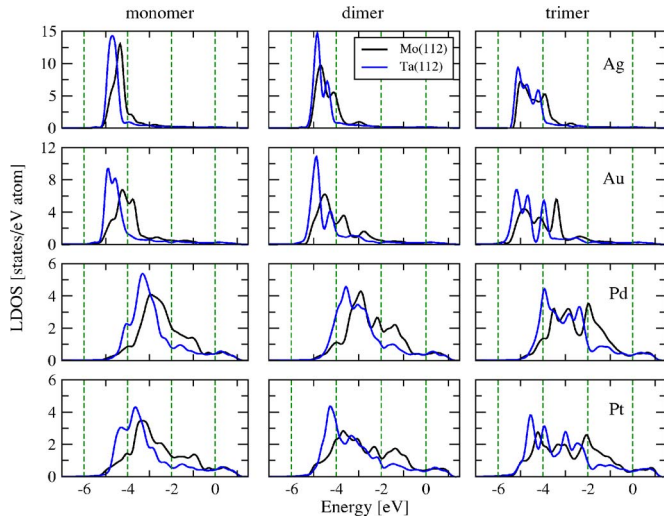


FIG. 5. (Color online) The local density of electronic states on Ag, Au, Pd, and Pt atoms adsorbed on Mo(112) and Ta(112). The states on a monomer, a dimer atom, and the central atom of a trimer are shown, respectively. Each row displays the LDOS on a different adatom. The energies are plotted relative to the Fermi level.

chains, which would mean that depolarization is larger for the sparser structures. For 0.2 ML the amount of this reduction varies between 0.01 D for the Ag/Mo and Au/Ta systems, to about 0.08 D for Au/Mo, Pd/Ta, and Pt/Ta. This again can be rationalized in terms of the electron smoothing effect which should be more efficient for the compact chain structures, and thus contributes to a more metallic character of the adatom bonding.

C. Electronic structure

To see the trend in the adsorbate binding properties at the two substrates, we compare in Fig. 5 the local density of states (LDOS) of monomer, dimer, and trimer atoms. In all cases the densities of states are dominated by d bands so we limit our discussion to the d -state behavior. We first look at the LDOS of individual adatoms. For Ag and Au metals the d states are fully occupied while the d bands of Pd and Pt are not completely filled, showing a substantial density of unoccupied states up to 1.5 eV. The Ag and Au d LDOS are narrower in energy (~ 1.5 – 2 eV) compared to Pd and Pt. All peaks on Ta are narrower than on Mo(112) and are shifted to lower energy. The features of both Pd and Pt on Ta(112) agree well with the experimental photoemission curves for Pd and Pt on Ta(110),²⁶ showing additional intense peaks at -4 and -4.5 eV below the Fermi level, respectively. For single atom adsorption the center of gravity of the LDOS on Ta is shifted down by 0.4 – 0.6 eV compared to that on Mo. This explains the stronger bonding of adatoms to the Ta(112) substrate (Table II). The peaks on the dimer atoms become broader and split, showing a shift of the electron band to higher energies. This is even more visible for the peaks on a trimer, in particular on the Mo(112). For the central atom in Au, Pd, and Pt trimers the intensity of the d LDOS is increasing in the region of higher energy (closer to the Fermi level)

TABLE V. Total and l decomposed valence charge in the atomic spheres (of radius 1.37 Å) around the Pd atoms adsorbed on Mo(112) and Ta(112) surfaces. The structures a–f refer to Fig. 1. For the triple adatom structures the charges on a central atom are presented.

Coverage	Case	Charge ($ e /\text{sphere}$)			Total
		s	p	d	
Mo surface					
1/10	a	0.374	0.136	8.159	8.669
2/10	b	0.374	0.136	8.158	8.668
	c	0.367	0.136	8.155	8.658
	d	0.364	0.155	8.138	8.657
3/10	e	0.366	0.138	8.158	8.662
	f	0.363	0.169	8.122	8.654
Ta surface					
1/10	a	0.414	0.175	8.116	8.705
2/10	b	0.411	0.172	8.121	8.704
	c	0.420	0.174	8.129	8.723
	d	0.403	0.192	8.110	8.706
3/10	e	0.413	0.180	8.110	8.704
	f	0.390	0.201	8.109	8.700

at Mo(112), while at Ta(112) it is highest in the low-energy region. On Ta, the LDOSs of the adsorbate atoms have a structure (multiple peaks for atoms of dimers and trimers) at lower energies than on Mo. This indicates a stronger adsorbate-adsorbate interaction and the tendency of chain formation on Mo. It also explains the domination of adatom-substrate coupling at Ta(112) and the preference for scattered adsorbate structures. Thus, similarly as for the Cu adsorption on vicinal surfaces of Mo and W,³⁴ the different adsorbate-substrate coupling is determined by the relative position of the d LDOS on Mo and Ta surfaces.

Additional information related to the LDOS is given by the amount of charge on the adatoms. The valence charge was calculated in a sphere of atomic radius drawn around every atom in various structures at the two different substrates. The results for Pd adatoms on the Mo(112) and Ta(112) surfaces are listed in Table V. The charges on the other adsorbates display similar trends. For all the adatoms and structures there is a significantly larger charge on adatoms at the Ta surface. The charge gain on adsorbate atom varies from 0.02, for Ag/Ta, to 0.07 $|e|/\text{sphere}$ for Pt/Ta compared to the Mo surface. Let us note that the total charge on an adatom is almost independent of the coverage (Table V). For the sparse adatom structures also the individual s , p , and d charge terms at the adsorbate do not alter. However, these components change quite significantly on the atoms forming the chains. In particular the p component on one of the dimer, and trimer atoms on Mo(112), changes by 14% and 24% respectively, compared to the charge on the Pd monomer. Similar but reduced p -charge enhancement (10% and 15%, respectively) is observed for Pd/Ta(112). A smaller increase in the adatom p charge at the Ta surface

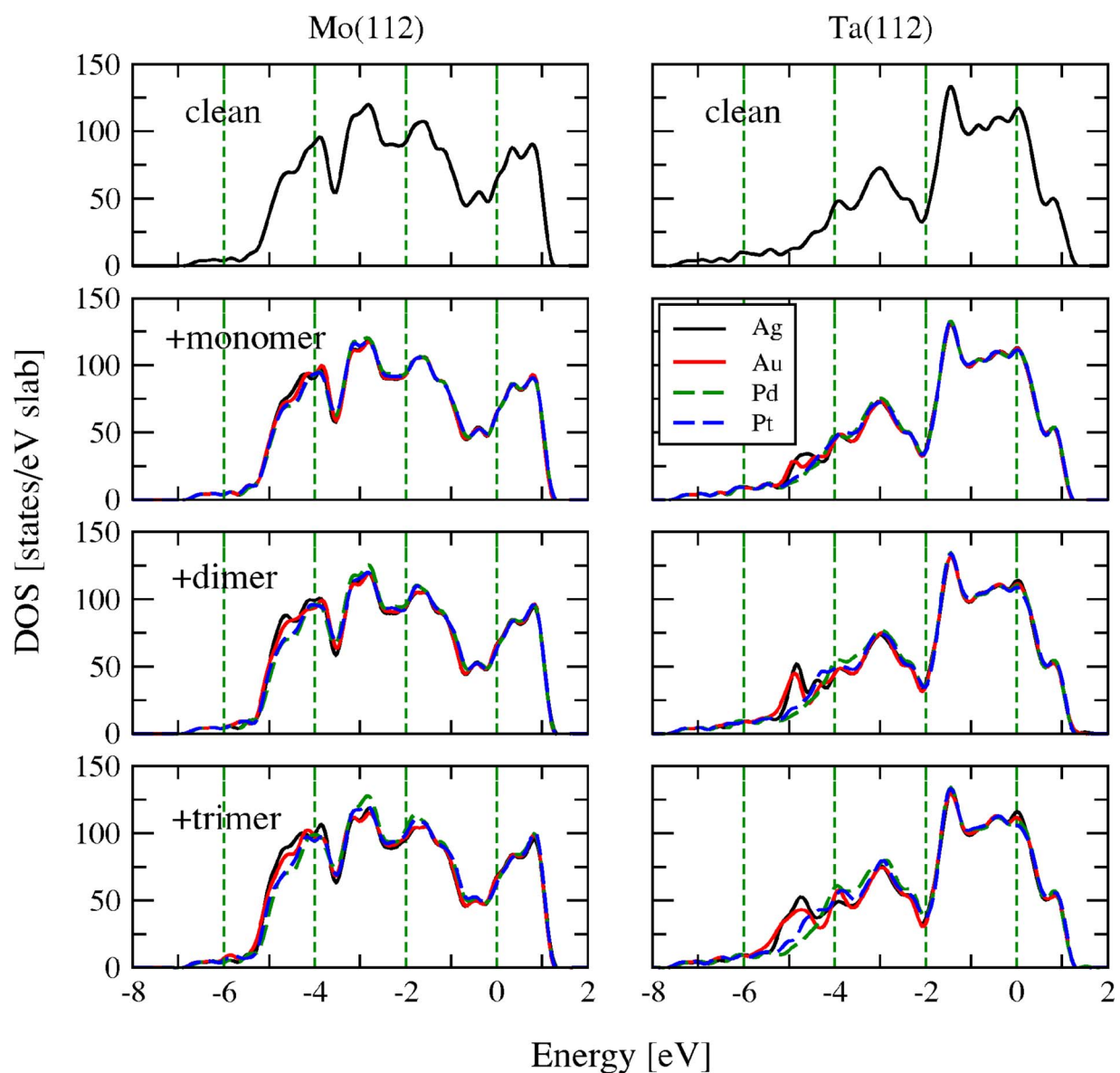


FIG. 6. (Color online) The full density of electronic states for the clean and adsorbate-covered (Ag, Au, Pd, Pt) Mo(112) and Ta(112) slabs.

may explain why the chain structures are not favored there. This charge is responsible for the binding. On the Ta surface the sp -charge rearrangement is not sufficient to form a metallic bonding which would compensate for the repulsive dipole-dipole interaction. Consequently, the lateral repulsion of the dipoles, with a possible contribution from the substrate-mediated indirect interactions,³⁶ leads to the formation of the sparse structures.

Figure 6 displays the full density of states (DOS) in the whole slab, for both clean and adsorbate-covered surfaces. The bandwidth is similar for the two substrates. However, the DOS of Ta is much lower in the energy region between -5 and -2 eV, to which the adsorbate's d states contribute most. The adsorbate d -state features are rather delocalized in the range of -5 and -1.5 eV, on Mo(112), while at Ta(112) the adsorbate states are localized in the energy range -5.5 to -3 eV, showing in particular the Ag and Au features which

fall in the lower-energy range (Fig. 5). A noticeable modification of the d states at the Fermi level by adsorbates is seen on Ta(112) which does not appear in the Mo(112) DOS spectrum.

D. Alloying

It is known that Pd and Mo, and Pt and Ta alloy not only in the bulk³⁵ but they also form surface alloys.^{24,37} In Ref. 37 the formation of an ordered Pd-Mo alloy at Mo(100) at half monolayer coverage was predicted. In order to get some indications about the possibility of formation of substitutional surface alloy at low coverages, we have exchanged the site of one of the adsorbed Pd atoms with the neighboring Mo atom of the topmost row (Fig. 1). This gives an information on an activation barrier (which could be overcome at elevated temperature) and represents the first step in alloy for-

mation. It should be noted that here we are interested only in the relative stability of the considered systems and not in the calculation of the absolute alloy formation energy. The latter would require consideration of the process in which one of the surface atom is substituted by an adsorbate atom and subsequently gets rebound at a kink site at surface step.¹⁸

For 0.1 and 0.2 ML coverage, the structures with atoms in exchanged sites are distinctly less favored (by 0.88 and 1.72 eV per supercell, respectively). Consequently, the formation of a surface Pd-Mo alloy is clearly excluded at these coverages. The energy difference per adatom slightly decreases with increasing coverage, which suggest that a critical coverage greater than that considered here is needed to induce the formation of an alloy. This is similar to the Pd/W(112) system where alloying, connected with migration of W atoms into adsorbate layer, was experimentally³¹ found only at 5 ML of Pd. Also, theoretically, the onset of Pd-W alloy formation requires a thicker Pd film compared to that needed for a Pt-W alloy.³⁸ The situation is different for Pd and Pt adsorption on Ta. For 0.1 ML of Pd on Ta the exchanged structure is only by 0.017 eV less stable than the original one. This suggests that Pd-Ta alloying is quite likely. For Pt on Ta, a similar exchange structure is by 0.155 eV more favored than the original one. For 0.2 ML of Pt on Ta(112) [Fig. 5, pattern (c)] the adsorbed and the alloyed structures (with adsorbed atoms replaced by the Ta atoms of uppermost rows, and vice versa) have the same energy, within the limits of the accuracy of our calculations. Thus, our results confirm the formation of a surface Pt-Ta alloy²⁴ at low coverages and indicate the possibility of Pd-Ta surface alloying at higher coverages. The electronegativities of Pt (2.3), Pd (2.2), and Mo (2.16), Ta (1.53) suggest that electron transfer from Pd, Pt to Ta is likely but not to Mo. A Pd or Pt atom among the atoms of the Ta(112) surface provides extra electron density to the “electron deficient” Ta surface atoms, thus stabilizing the system. Calculations of the electron charge confined in the atomic spheres around the atoms provide evidence for the electron charge loss at the Pd or Pt atom that replaced one of the Ta surface atoms, and the charge gain at the Pd atom immersed in the Mo surface.

IV. SUMMARY

The structure and energetics of various configurations of Ag, Au, Pd, and Pt atoms adsorbed on the relaxed (112) surface of Mo and Ta are presented and discussed. We found that adsorption of these atoms has a stabilizing effect on the Mo and the Ta (112) surface, which is manifested in a reduced topmost layer relaxation. The binding energy of Ag, Au, Pd, and Pt atoms in compact chain structures on Mo(112) increases with coverage. Ag, Au, Pd, and Pt atoms are by 0.2–1 eV more strongly bound to the Ta than to the Mo(112) substrate. In-trough dimers of the Ag, Au, Pd, and Pt on Mo(112) are by 25–65 meV favored over random adatom structures. Corresponding linear trimers are more stable by 0.05–0.2 eV than separated structures. The calculated increase of the work function at low adatom coverages is consistent with the measured trends for the Mo and the Ta(112) systems. Formation of transition metal adatom chains on Ta(112) is unfavored. Thus, it appears that it is the electronic properties of the substrate that determine the tendency of adatoms to chain formation in the first place. The differences in the calculated binding energies of adatoms belonging at the same coverage to compact and sparse structures show that for Ag and Au atoms on Ta(112) the repulsive interactions are much stronger than for Pd and Pt. Consequently, any clustering of Ag and Au on the Ta surface is less likely than for Pd and Pt. Our results indicate that at low coverages Pd and Pt atoms mix with Ta(112) surface atoms.

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