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2002 J. Phys.: Condens. Matter 14 L273

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LETTER TO THE EDITOR

Variation of adatom to substrate charge transfer value along the first-row transition metal series on Mo(110)

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Received 14 December 2001

Published 15 March 2002

Online at stacks.iop.org/JPhysCM/14/L273

Abstract

Adsorption of the first-row transition 3d metals (Ti–Cu) on the atomically clean Mo(110) surface in ultra-high-vacuum conditions has been studied by Auger electron spectroscopy and work function measurements (Anderson method). In this letter it is shown that adsorption behaviour of the metals under consideration systematically changes along the 3d series. The observed correlation between the systematic change of the dipole moments and the values of the charge transfer from adatom to substrate along the period leads us to the conclusion that the metal 3d orbitals play an important role in the formation of the chemisorption bond.

Adsorption of metal atoms on smooth atomically clean substrates is one of the most extensively studied areas of surface science [1]. It is known that charge transfer upon chemisorption strongly affects the properties of the interface [2]. This, in its turn, opens the possibility of fabrication of materials suitable for specific technological application. For instance, in the case of the Ni/Mo system the charge transfer from Ni to Mo plays an important role for increasing catalytic action in the hydrodesulfurization (HDS) process [3]. Previous XPS results of Campbell [4] show that in adsorption of Ni on Mo(110) the core levels of both Ni 2p and Mo 3d shift to higher binding energy. To account for this shift Kuhn and Rodriguez [5] on the basis of theoretical calculations suggested that a complex process of a Mo(4d) → Mo(5s, 5p) rehybridization following a Ni(3d, 4s) → Mo(5s, 5p) electron transfer occurs. These, as well as a variety of other data [2], point to the decisive role of the adatom's d electrons in the formation of chemisorption bonds with the substrate. For further elucidation of the role of these electrons in chemisorption, systematic measurements for the entire transition metal series carried out in the same experimental conditions would be useful. This is why the aim of the present study

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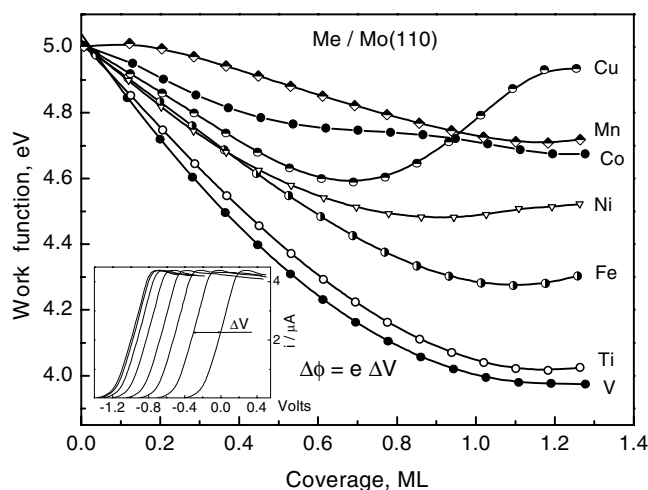


Figure 1. The work function versus coverage plots for 3d metals on the Mo(110) surface measured by the Anderson method. The substrate temperature during the metal adsorption is 300 K. A series of retarding curves for Ti deposition is shown in an inset.

is the experimental investigation of adsorption of first-row transition metal atoms (Ti–Cu) on the Mo(110) surface.

Measurements have been carried out in a UHV chamber (base pressure $<10^{-10}$ Torr) by means of Auger electron spectroscopy (AES) and work function measurements. For AES a double-pass cylindrical mirror analyser with coaxial gun operating at a primary energy of 3 keV and beam current of $0.1 \mu\text{A}$ was used [6]. The spectra were recorded both in $N(E)$ and dN/dE mode. The work function change ($\Delta\phi$) was measured by the Anderson method [7]. For this purpose a special electron gun operating at low primary beam energy (1–10 eV) was mounted in the vacuum chamber. The retarding curves, that is the plots of collected current (i) versus the retarding potential (U) as the sample undergoes a work function change, were measured completely over the entire range of accessible values of U (–5 to 5 V). For example, a series of retarding curves for Ti deposition on Mo(110) are shown in an inset of figure 1. A mechanically and electrolytically polished Mo(110) sample was fixed at the sample holder, allowing heating by electron bombardment. The Mo(110) surface was cleaned by the usual procedure of heating (1200 K) in an oxygen ambient at 10^{-6} Torr for 20 min with subsequent high-temperature flashing to 2500 K after closing the oxygen doser. The ultrathin films of all the transition metals were deposited by thermal evaporation of corresponding bulk materials with 99.97–99.99% purity. The growth rate and the coverage of the films were estimated by Mo MNV (188 eV) Auger intensity signal attenuation with account of inelastic mean free paths of the electrons in the respective film [8], as well as by quartz microbalance. We estimate the error in measuring the film coverage (θ) at 15–20%. The coverage was assumed to be equal to unity ($\theta = 1$) when surface concentrations of adatoms and atoms on the Mo(110) surface ($1.43 \times 10^{15} \text{ cm}^{-2}$) coincide. Experimental details and procedures are described in more detail elsewhere [6,9–11].

The growth of 3d metals on refractory metal surfaces at submonolayer to multilayer coverage has been quite extensively studied in recent decades [12–16]. In almost all reported cases the layer-by-layer growth mode occurs at least up to 3–5 ML. A similar growth mode was also observed in the present case: Auger uptake curves for all the metals studied exhibit a linear change of the Auger intensity of both adsorbates and the substrate until the completion of the first monolayer, which is indicative of complete monolayer formation [12]. Subsequent

increase of the coverage also allows a linear fit (at a different slope) of the experimental points up to 2 ML, except Cr and Co, for which deviation from linearity at $\theta > 1$ is observed. Complete monolayer formation is consistent with the thermodynamic argument that the free surface energy of 3d metals (1200–1700 erg cm⁻²) is considerably lower than those for Mo(110), W(110), Ta(110) or Re(1000) (3000 and 4000 erg cm⁻²) [17], thus resulting in wetting of the substrate by the film. According to numerous literature data, increasing metal coverage on Mo(110), as well as on W(110), Ta(110) and Re(1000), results in a sequence of different types of superstructure, which are attributed to the different lattice mismatches between film and substrate [18]. The common feature for all 3d metals is that at a coverage close to or slightly above unity the film takes a structure resembling the close-packed face of the corresponding metal, that is (1000) for Ti, (110) for V, Cr, Mn and Fe and (111) for Ni, Co and Cu. However, despite this similarity the structures of the film and the respective bulk crystal still exhibit quite noticeable differences, manifesting themselves, for instance, in that the film can possess quite a high stress (up to 1.0 N m⁻¹ [19]) originating from different lattice mismatches between film and substrate. In an extension of existing models for heteroepitaxial growth it is suggested that adsorbate-induced modifications of the electronic structure at the film/substrate interface dominate the formation of the structure and thus the stress in the submonolayer range [19].

In this letter it is demonstrated that during submonolayer film growth of 3d metals on Mo(110) the electronic properties of the metal/substrate interface change with adatom coverage and that the 3d-orbital filling plays an important role in the formation of the electronic properties of the metal/substrate interface. Work function versus coverage plots for 3d metals on Mo(110) normalized to the same coverage are shown in figure 1. The work function change is proportional to the shift of the linear part of the retarding curve ΔV (figure 1, inset). Assuming that the work function of Mo(110) is equal to 5.0 [20], it is possible to plot the absolute values of the work function. It is seen that, depending on the metal, the work function changes in a markedly different way. This is different from what is measured for alkali, alkali- and rare-earth (4f-series) metals, in which case the work function versus coverage plots are generally similar: a steep initial drop followed by quite a deep minimum (0.5–1.5 eV) and a subsequent saturation region [21, 22]. Likewise, as a consequence of weak participation of 4f electrons in the formation of chemisorption bonds along the 4f-series metals on Mo(110) and W(110) surfaces, the absolute values of ϕ versus coverage plots are quite close to each other [23]. Unlike this, different characters of the work function change along the 3d-metal series (figure 1), providing evidence, consistent with earlier theoretical calculations [24], that 3d electrons play an important role in the formation of the electronic structure of the metal/substrate interface.

The common feature for all the metals is that the work function stabilizes at a coverage close to unity. Moreover, the stationary values of ϕ are in rough agreement with the values reported for corresponding bulk crystal close-packed surfaces [25]. This may be a brief indication that the electronic properties of the monolayer films resemble in a certain respect the properties of the bulk metals. It should be noted, however, that some properties of the films are not formed at one monolayer and need at least 3–8 ML. For instance, Rodriguez and Goodman [26] have shown that monolayer depositions of dissimilar metals can lead to surfaces with different catalytic properties compared with the surface layer of the same bulk metal. Also, in our previous infrared spectroscopic measurement on nitric oxide (NO) adsorption on Ni(111) film formed on W(110) we observed that the vibrational spectra of NO on the Ni film correspond to those measured for NO on bulk Ni(111) crystal at an Ni film thickness of 4 ML [27]. Decrease of the work function for all the metals studied is in agreement with the relationship between the electronegativities of the adatoms and the Mo(110) surface [28]. The former are systematically lower than the electronegativity of Mo(110). This makes the adatoms' valence electronic charge polarized

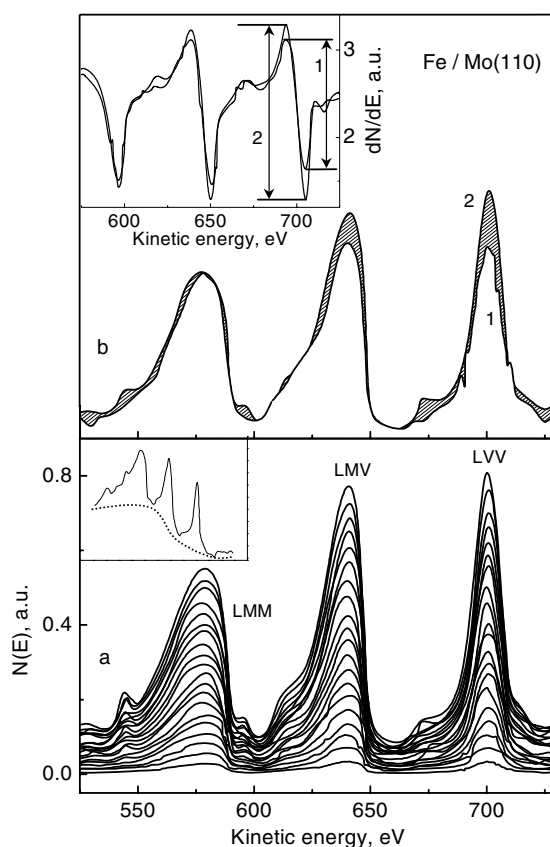


Figure 2. (a) A series of integrated background-subtracted Auger spectra for Fe/Mo(110) at Fe coverage beginning from 0.05 ML and successively increasing by 0.1 ML. Measured spectra with the background drawn are shown in an inset. (b) Comparison of the Fe spectra at an Fe coverage of 0.05 (curve 1) and 2 ML (curve 2) normalized to the same LMM intensity. The corresponding differentiated spectra are shown in an inset. The filled area shows the relative difference between the peak areas of LVV, LMV and LMM transitions.

towards the substrate, thus creating an effective dipole layer. Assuming the validity of the dipole model of the work function change, one can estimate the initial (that is at $\theta \rightarrow 0$) dipole moments (μ) of chemisorption charge by the Helmholtz equation ($\Delta\phi = 4\pi e\theta\mu$). These are 0.70, 0.75, 0.40, 0.0, 0.30, 0.10, 0.20 and 0.15 D for Ti, V, Cr, Mn, Fe, Co, Ni and Cu, respectively. A general tendency of dipole moment decrease (except for V and Mn) along the 3d series is consistent with both the electronegativity increase and atomic polarizability decrease in the same sequence [28]. The shape of $\phi(\theta)$ plots suggests that the dipole moments decrease as coverage grows. A common explanation of such behaviour is the mutual depolarization of adatoms [22].

Apart from the work function decrease, the shift of adsorbate valence electronic charge towards the substrate is also reflected in the way the Auger electron spectra change with the coverage increase. For example, a series of integrated background-subtracted LVV–LMM Auger spectra of Fe successively deposited on Mo(110) at equal quantities of 0.1 ML beginning from Fe coverage of 0.05 ML is shown in figure 2(a). The background of the measured spectra (see inset) was subtracted according to the procedure proposed recently for 3d metals [29]. Analysis of the Auger spectrum series demonstrates that the peak areas of LVV, LMV and

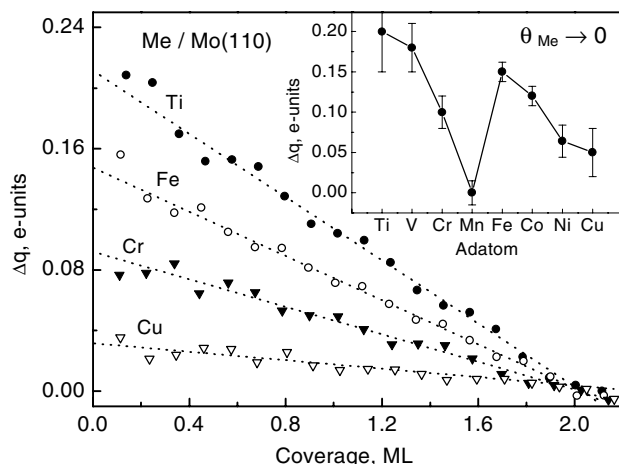


Figure 3. The value of chemisorption charge transfer (Δq) versus coverage for Ti, Fe, Cr and Cu on Mo(110). Extrapolating these plots to zero coverage gives an estimate of values of Δq for single adsorbed atoms. Variation of these values along the 3d series is shown in an inset.

LMM transitions evolve in a different way as the coverage increases. Comparison of the spectra normalized to the same LMM intensity at a metal coverage of 0.05 and 2 ML shows this difference (figure 2(b)): with increasing coverage the LVV and LMV intensities increase faster than the LMM intensity, as indicated by the filled area. This is also confirmed by comparison of the corresponding differentiated spectra (figure 2(b), inset). Such a tendency holds for all the metals studied, except Mn.

The intensity of Auger emission from the valence level (as well as any other level) is proportional to the value of the electronic charge at this level, and the observed behaviour of the spectra can be explained, assuming that the value of the charge at the adsorbate valence level is lower at the lower coverage than at the higher coverage. To make a quantitative estimate it is informative to recall the earlier result of Allen *et al* [30], suggesting that for the entire 3d series of metals the following relationship holds:

$$R = A(\text{LVV})/A(\text{LMM}) = Cq(q - 1), \quad (1)$$

where $A(\text{LVV})$ and $A(\text{LMM})$ are the corresponding peak areas, q is the charge (number of electrons) at the valence level of the metal and C is a constant value. When a metal adsorbs on a substrate surface the value of its valence level electronic charge changes by the value of Δq due to the formation of a chemisorption bond. According to the above-mentioned work function results, for the systems under consideration the chemisorption charge polarizes towards the substrate. In this case the above relationship should acquire the following form:

$$R = C(q - \Delta q)(q - \Delta q - 1). \quad (2)$$

For all the adsorbates studied (except Mn) the Auger ratio (R) versus coverage plots exhibit a gradual increase until saturation at about 2 ML. Assuming that at this coverage the properties of the overlayer are in a certain respect close to the properties of the bulk metal, it is reasonable to consider that $\Delta q = 0$, that is the metal atom in the film does not have an excess valence charge compared with the bulk metal atom. This allows us to determine the value of constant C , and subsequently build the absolute Δq value versus coverage plots. As an example, such plots for Ti, Fe, Cr and Cu are shown in figure 3. It is seen that the adatom to substrate electronic charge transfer Δq decreases as the coverage grows, which corresponds to the

above-mentioned decrease of the dipole moments with coverage increase. Although, because of the limited sensitivity, AES does not allow us to reliably measure the spectra at very low coverage, it is, nevertheless, possible to estimate the absolute values of electronic charges of single adsorbed atoms by extrapolating the $\Delta q(\theta)$ dependences to zero coverage. These values are (if measured in electron charge units) 0.20, 0.18, 0.10, 0.0, 0.15, 0.12, 0.07 and 0.05 for Ti, V, Cr, Mn, Fe, Co, Ni and Cu, respectively. They are considerably lower than those reported for alkali and alkali-earth metal atoms adsorbed on refractory metal surfaces [21, 22]. The latter are in the range of 0.7–1.0. In this regard the 3d metal to substrate chemisorption bond cannot be viewed as ionic. However, despite such a difference the adsorption energy of 3d metals is not much lower than that for alkali metals, suggesting formation of a strong interfacial bond [4, 5, 12]. Therefore, it might be reasonable to expect that the chemisorption bond has mainly covalent character with some polarization of the charge towards the substrate [4, 5]. As the metal coverage increases, adatom to substrate polarization, and hence Δq , decreases (figure 3), most likely due to the formation of lateral bonds between adatoms. Together with the values of the dipole moments, the values of Δq of single adatoms systematically vary along the 3d series. The corresponding plot is shown in an inset of figure 3. Such systematic dependence may serve as an indication of considerable participation of 3d electrons in the chemisorption bond formation. That the Mn, and, to a certain extent, Cr violate the gradual tendency of Δq decrease along the series (inset of figure 3) may be attributed to the fact that the half-filled d shells exhibit relative stability towards charge transfer and polarization [5, 24]. The stronger correlation effects exhibited by the d^5s^2 [24, 31] electronic configuration can also explain the exceptional behaviour of Mn ($3d^54s^2$). The shape of $\phi(\theta)$ plots (figure 1) suggests that at coverage lower than 0.2–0.3 ML the work function for most metals decreases almost linearly, implying that the dipole moments of the chemisorption bond do not change considerably. At the same time the value of the corresponding charge transfer decreases with the coverage increase (figure 3). These facts allow us to assume that there is an increase of the adsorbate/substrate interlayer distance with the coverage, at least in the indicated coverage range. The chemisorption charge transfer allows us to estimate the relative chemisorption bond spatial expansion for 3d metals on Mo(110) with the coverage at 0–0.3 ML: depending on the metal they are in the range 3–7%. A similar trend is reported for alkali metals adsorbed on the metal surfaces, in which case, however, the effect is much more apparent: the metal/substrate interlayer distance relaxation can be as much as 30–40% [32].

In conclusion, it is shown that electronic properties of 3d-metal/Mo(110) adsorbate systems systematically change along the period, excluding Mn. Assuming that 3d orbitals play a decisive role in the formation of chemisorption bonds, this systematic change can be attributed to the gradual 3d-level filling of the metals. Apart from determining the dipole moments of adatoms, the absolute values of electronic charge transfer from adsorbate to substrate are estimated for the entire first-row transition metal series (excluding Sc) on Mo(110).

One of the authors (TM) gratefully acknowledges research grants from European Union Science Committee and Deutscher Akademischer Austauschdienst (DAAD). The authors express their thanks to Professors Yoshitada Murata and Katsuyuki Fukutani for their cooperation, and David Remar and Naomi McLeod for technical assistance.

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