

Surface distribution of Cu adatoms deduced from work function measurements

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We report on work-function changes due to Cu impurities on 1-ML Xe adsorbed on highly oriented pyrolytic graphite, as determined by normal-emission ultraviolet photoelectron spectroscopy. The dipole moment and polarizability of a single Cu impurity are deduced from the measurements within the Topping model. The results indicate that Cu atoms adsorb as isolated impurities, a picture which is supported by density-functional calculations. This finding confirms an earlier assumption in the scenario for the appearance of a Fano resonance in valence-band photoemission spectra.

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I. INTRODUCTION

Recently, the observation of a Fano resonance in ultraviolet photoelectron spectroscopy (UPS) was reported for the system Cu/Xe/HOPG (highly oriented pyrolytic graphite).^{1,2} Below 50 K, 1 ML of Xe forms a commensurate overlayer on the HOPG surface, leading to a folding of the graphite π -band by coupling the K point of the graphite Brillouin zone with the Γ point of the Xe layer zone. This projection induces considerable spectral density between the Fermi level E_F and 2-eV binding energy in normal-emission UPS spectra. After subsequent deposition of 0.1-ML Cu, a pronounced Fano resonance profile is observed in the photoelectron spectra. The resonance has been attributed to the interference between the graphite π -band continuum and the discrete Cu $4s$ atomiclike level. In this interpretation the Cu atoms are considered as isolated impurities in the Xe layer.

In order to test this assumption experimentally, we performed a work function (WF) study as a function of Cu adatom concentration on Xe/HOPG. We show that WF measurements are well suited to deduce the mobility and the adatom distribution of the Cu atoms in the low concentration limit.

In general, the adsorption of atoms or molecules onto a surface causes a change of the charge distribution at the surface, leading to the creation of a surface dipole layer. As a consequence, a modification of the WF is observed. The sign and amplitude of this variation depend on both the adsorbed species and the substrate and on the mobility of the adsorbed atoms. The sign of the WF change indicates the direction of the charge transfer or, more generally, of the charge redistribution. A lowering of the WF corresponds to a net positive charge at the surface, while an increase of the WF is the consequence of a negative dipole. Moreover, the magnitude of this WF change depends on the concentration of the adsorbate.

Topping³ developed an expression for the mutual potential energy of a distribution of electric dipoles lying in a plane (with their axis perpendicular to the plane) as a function of their density. Based on these calculations, a quantitative relationship between the work function and the adsor-

bate concentration was derived.⁴ Adsorbates are treated as individual dipoles at the surface, and their subsequent depolarization as a function of concentration is taken into account. Such systems, where the adatoms remain isolated on the surface, are generally realized at low adatom concentrations in the absence of surface diffusion or in the presence of mutual repulsion. Important physical quantities, like the dipole moment (p_0) and the polarizability (α) of a single adsorbed atom, may be derived within this model.

When the adatom concentration approaches 1 ML, the presence of surface diffusion and of an attractive interaction between the adsorbates leads to clustering and island formation. In this case the Topping model is much less appropriate to describe the WF trend. As a remedy, e.g., a concentration-dependent polarizability was introduced recently.⁵

In the past, the Topping model was successfully applied to various adsorbate-substrate systems, e.g., K on W,⁶ rare-gas atoms on Al(111),⁷ and alkali metals on a semiconductor surface.⁸ For example, due to a small charge redistribution, physisorbed Ar, Kr, and Xe on Al(111) display only a very small dipole moment p_0 , which in turn corresponds to weak adsorbate-surface bonding. On the other hand, for Li and Cs on CdTe(100) the strong dipole moment corresponds to a net charge transfer from the adsorbate to the substrate indicating considerable bonding.

In this paper we show the results of our WF measurements for the system Cu/Xe/HOPG. Then we compare these measurements with the observations made for the related systems: Cu/Kr/HOPG, Cu/Ar/HOPG, and Cu/HOPG. For Cu/Xe/HOPG we analyze the WF data within the Topping model, and deduce the dipole moment and polarizability of a single Cu impurity. We conclude that the Cu impurities are randomly distributed, and that they remain isolated in the Xe layer.

II. EXPERIMENT

The experiments were performed in an ultrahigh-vacuum chamber (base pressure: 1×10^{-10} mbar) equipped for UPS, x-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy, and low-energy electron diffraction. A high-

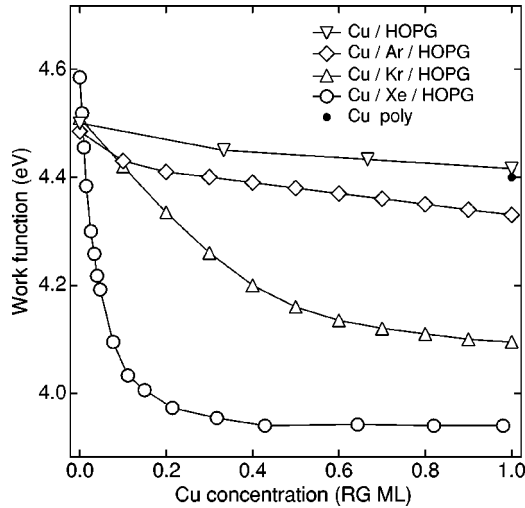


FIG. 1. Measured WF changes as a function of Cu concentration for: Cu/HOPG (∇), Cu/Ar/HOPG (\diamond), Cu/Kr/HOPG (\triangle), and Cu/Xe/HOPG (\circ), up to 1 RG ML of nominal concentration, where 1 RG ML corresponds to 0.36 Cu(111) ML. The continuous lines to guide the eye. Also indicated (\bullet) is the value of the WF for a Cu polycrystalline sample. A typical error bar on the WF values is of ± 0.02 eV.

intensity gas discharge lamp (Gammadata) combined with a home-built monochromator allows us to measure satellite-free spectra. The spectra are excited by the main resonance lines: He I (21.2 eV) and He II (40.8 eV). The photoemitted electrons are collected by a hemispherical analyser (HA 150 from VSW), with an angular resolution of $\pm 2^\circ$, and a total instrumental energy resolution set to 50 meV. The WF was determined by applying a negative voltage to the sample and by measuring the secondary electron onset E_{onset} . Knowing the Fermi-level position E_F , we define $\Delta E = E_F - E_{onset}$ as the energy width of the photoemitted spectra. The WF of the sample is then obtained by $e\phi = h\nu - \Delta E$, where $h\nu$ is the photon energy.

The HOPG substrate, freshly cleaved, was mounted on a cold finger held at $T = 50$ K by a closed-cycle He refrigerator. The temperature was measured by means of a thermocouple fixed on the sample holder. A retractable electron gun allows the rapid heating of the sample up to 1200 K for the cleaning procedure. Xe (Kr, Ar) was introduced in the vacuum chamber by a leak valve, and adsorbed on the HOPG substrate at low temperature. The thickness of the Xe (Kr, Ar) layer was determined from the typical emission from the Xe $5p$ (Kr $4p$, Ar $3p$) levels.⁹ Cu was deposited from a directly heated tungsten filament. The Cu concentration was calibrated by XPS measurements of Cu $2p$, Xe $3d$, and C $1s$ core levels, with an accuracy of $\pm 10\%$.

III. RESULTS AND DISCUSSION

Figure 1 shows the results of the WF measured for Cu/HOPG (∇), Cu/Ar/HOPG (\diamond), Cu/Kr/HOPG (\triangle), and Cu/Xe/HOPG (\circ) as functions of the Cu concentration. In their commensurate phase, Xe, Kr, and Ar form the same ($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ superstructure on HOPG. The lattice parameter

of its unit cell is $d = 4.26$ Å. We express the concentration of adsorbed Cu in terms of this rare-gas (RG) ML. This corresponds to a much lower density of Cu atoms with respect to a Cu(111) surface. In fact, 1 RG ML corresponds to 0.064 atoms/Å², while 1 Cu(111) ML (with lattice parameter 2.56 Å) corresponds to 0.176 atoms/Å². This means that 1 RG ML = 0.36 Cu(111) ML.

Deposition of Cu directly on HOPG gives rise to a smooth change in the WF. In this case the Cu atoms diffuse at the surface forming metallic islands¹⁰ and the WF tends to the value measured for a polycrystalline Cu surface (\bullet). Cu deposition on Xe/HOPG leads to an initial steep decrease in the WF followed by an asymptotic behavior with increasing Cu adatom concentration (see Fig. 1). The maximum WF change is about 0.6 eV. The initial WF decrease is less pronounced for Cu on Kr/HOPG, while the overall change in the WF is still about 0.4 eV. Finally, for Cu on Ar/HOPG, there is only a weak decrease in the WF as a function of Cu concentration. We assume that the different concentration dependent WF changes observed in Fig. 1 are caused by a difference in the mobility of the Cu atoms on the various RG layers. On the Ar layer the Cu adatoms diffuse almost as easily as on the bare HOPG substrate, while the Xe layer impedes diffusion and subsequent island formation. The Kr system represents an intermediate case.

We substantiate this interpretation by an analysis of our WF data for Cu/Xe/HOPG within the Topping model. The WF variation $e\Delta\phi$ may be described by¹¹

$$e\Delta\phi = \pm e \frac{p_0 n_a}{\epsilon_0} \left(1 + \frac{\alpha \xi \delta n_a^{3/2}}{4\pi\epsilon_0} \right)^{-1}, \quad (1)$$

where p_0 is the initial dipole moment of the single adsorbate, n_a is the density of adsorbed atoms, α denotes an effective polarizability, ξ is a constant related to the mutual interaction of the dipoles in the adsorption geometry, and δ is a parameter that takes into account the possible ordering in the sub-monolayer regime.¹² The atom density may be expressed as

$$n_a = \frac{\theta}{d^2} b, \quad (2)$$

where θ is the adsorbate coverage ($0 \leq \theta \leq 1$) and d is the lattice constant in the surface cell, i.e. the nearest-neighbor distance in the complete monolayer, so that d^2/b is the area of the surface unit cell; $b = 1$ for a square surface unit cell and $b = 2/\sqrt{3}$ for a triangular one. δ is a parameter that takes into account the mobility of the atoms at the surface. According to a lattice gas model,¹³ $\delta = \theta^{-0.5}$ means that the atoms are randomly distributed on the surface, while $\delta = \theta^0 = 1$ describes a uniform distribution of adsorbed atoms (the distance between the atoms is $d\theta^{-0.5}$).⁶

The linear term in Eq. (1) depends on the dipole moment p_0 , and takes into account only the adsorbate-substrate interaction (formation of the dipoles). Consequently it reflects the initial variation of the WF for low adsorbate concentration. The second term describes the depolarization due to the dipole-dipole interaction between the adatoms. The parameter ξ is a constant equal to 11.034 for a triangular lattice,

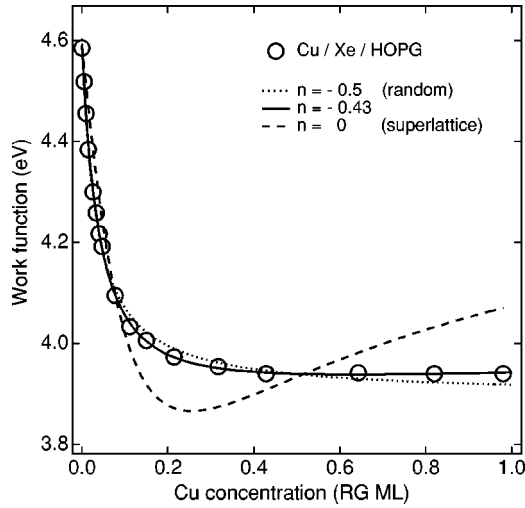


FIG. 2. Measured WF change as a function of Cu concentration on Xe/HOPG (\circ) and curves calculated with the Topping model. The dashed curve corresponds to a superstructure of isolated Cu atoms ($n=0$) and the dotted curve to a random distribution of Cu atoms ($n=-0.5$); the solid line represents the best fit ($n=-0.43$). Note that 1 RG ML corresponds to 0.36 Cu(111) ML.

and its value represents the sum of the contributions to the interaction of each pair of dipoles (a kind of Madelung constant, but calculated by Topping with a dipole-dipole interaction).³ Equation (1) may then be rewritten as

$$e\Delta\phi = \pm e \frac{p_0}{\epsilon_0} \frac{\theta b}{d^2} \left(1 + \frac{\alpha \xi}{4\pi\epsilon_0} \frac{\theta^n (\theta b)^{3/2}}{d^2} \right)^{-1}, \quad (1')$$

where we have expressed δ in terms of θ^n ($-0.5 \leq n \leq 0$), in order to include the dependence on the adatom mobility.

In Fig. 2 we show the results of a fit of this model to the WF data for Cu/Xe/HOPG. The dashed curve models an adatom superstructure of isolated Cu atoms ($\delta=1$, $n=0$), and





clearly disagrees with the experimental data. The dotted curve corresponds to a fully random distribution of the adsorbates ($n=-0.5$), and it closely describes the experimental data. The solid curve represents the best fit to the data with a parameter n differing slightly (14%) from the value appropriate for the random distribution scenario. Thus the mobility of the Cu atoms is strongly reduced, and they are randomly distributed in the Xe layer.

For the Cu impurities in the system Cu/Xe/HOPG we deduce a dipole moment p_0 of $1.5 \pm 0.2 e \text{ \AA}$.¹⁴ It is interesting to note that this large dipole moment is comparable to the values found for the dipole moments of alkali atoms on metal surfaces.⁴ In contrast, the case of Xe on Al(111) (Ref. 6) shows that if the adsorbate-substrate interaction is weak, the dipole moment is small: $0.049e \text{ \AA}$. Our data analysis yields a polarizability α of $140 \pm 15 \text{ \AA}^3$.¹⁶ The calculated value for the polarizability for isolated Cu atoms is much lower: 6.1 \AA^3 .¹⁵ However, the fact that the experimental values reported for alkali atoms (K or Rb) have the same order of magnitude¹⁵ indicates that the $4s$ outer shell of isolated Cu adatoms on Xe/HOPG shows a striking similarity to the one of alkali adatoms. The values found for the individual dipole moment p_0 and the polarizability α indicate that the Cu impurities on Xe/HOPG are similar to alkali impurities on metal surfaces.

In order to determine the microscopic structure from a theoretical point of view, we have investigated the system Cu on Xe/HOPG with DMol³ density functional calculations.^{17,18} In the calculations, the self-consistent field (SCF) is realized with a slab periodicity of 75 a.u.; k -point integrations are performed with a shifted $4 \times 4 \times 1$ mesh in all cases; a DMol³ DNP (Double Numerical basis set with Polarization function) is used with atomic cut-off at 8 au. Calculations were performed using the Perdew-Wang (PWC) local density functional.¹⁹ The results are resumed in Table I.

The starting system is a five layer graphite slab at experimental bulk geometry, covered with 1-ML Xe (no Cu ada-

TABLE I. Results of DMol³ density-functional calculations for the system Cu on Xe/HOPG. Each line corresponds to a different calculation; the schematic drawings show the different systems (top view); the graphite layers are not shown. (large circles: Xe atoms; gray circles: Cu atoms). Line 1: 1-ML Xe; line 2: 0.25-ML Cu substitutional to Xe atoms; line 3: 0.25-ML Cu sub-Xe layer (hollow site); line 4: 1-ML Cu sub-Xe layer (hollow site). Total energy (E_{tot}), and energy of the Cu atoms (E_{Cu}) resulting from the optimization are indicated for each calculation. $e\Delta\phi$ is the variation in the WF with respect to the value found for the starting system (line 1). h_{Xe} and h_{Cu} denote the distance of Xe and Cu atoms, respectively, from the center of the slab.

Line	System	$e\Delta\phi$ (eV)	E_{tot} (eV)	E_{Cu} (eV)	h_{Xe} (au)	h_{Cu} (au)
1	 1 ML Xe		1066.44		19.47	
2	 (0.25 ML Cu)(0.75 ML Xe)	-0.77	1066.93	0.49	19.37	16.33
3	 (0.25 ML Cu)(1 ML Xe)	-1.91	1068.67	2.23	3@19.34, 1@19.41	16.32
4	 (1 ML Cu)(1 ML Xe)	-1.80	1073.44	1.75	19.54	16.34

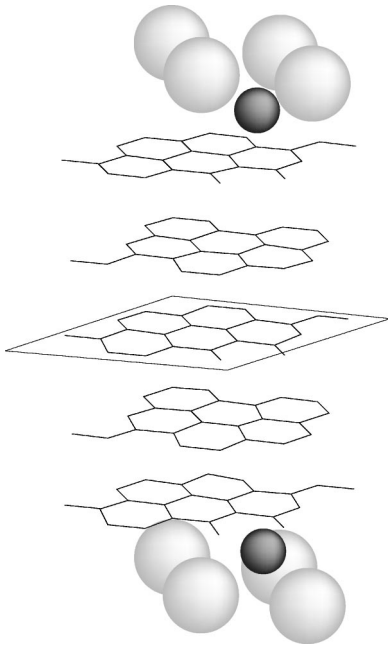


FIG. 3. Central part of the repeated slab cell, containing 130 atoms, used in the calculation (0.25-ML Cu)(1-ML Xe) (Table I, line 3). The total height of the cell (corresponding to the slab periodicity used) is 75 a.u., while the thickness of the slab is approximately 40 a.u. Both sides of a five-layer graphite slab are covered with Xe (large white spheres) and, below the Xe surface, with 0.25-ML Cu (grey spheres) in a hollow site.

toms) (line 1). The use of adatoms placed symmetrically on both sides eliminates long-range electric fields from the back of the slab. The carbon atoms are kept fixed at the bulk graphite positions during optimization of the adsorbate.¹⁸ The bulk geometry we used gives 12.85 a.u. for the height of the top layer carbon above the slab center. The second system we have studied consists of 0.25 ML of Cu substituting Xe atoms (line 2 in Table I). The position of the Fermi energy suggests a WF lowering of 0.77 eV with respect to the starting system. The next calculation is done for 0.25 ML of Cu on 1-ML Xe (line 3). This optimization required the use of thermal occupations with an artificial electron temperature.²⁰ The calculation was started with Cu in a top layer in a hollow site, and the optimized final position is sub-Xe surface, as indicated by the value of h_{Cu} , which represents the optimized distance of the Cu adatom from the center of the slab.

The reoptimization with Cu below the Xe layer was done with zero temperature again (see Fig. 3, line 3). The result of these simulations strongly suggests that the Cu adatom is more stable than the Xe-substitutional Cu atom, as indicated by the values for the total energy E_{tot} for the systems of lines 2 and 3. These values for E_{tot} also suggest that it is energetically favorable for the system to keep the Xe layer on top.²¹ Interestingly, the adatom Cu ends up in a sub-Xe surface position (line 3), which was somewhat unexpected. The 1-ML Cu 1-ML Xe (line 4) is less bound than the 0.25 ML Cu, suggesting a tendency against the formation of Cu islands. Calculations for all Cu on Xe/HOPG systems yield a very significantly lowered WF as compared to Xe on HOPG,

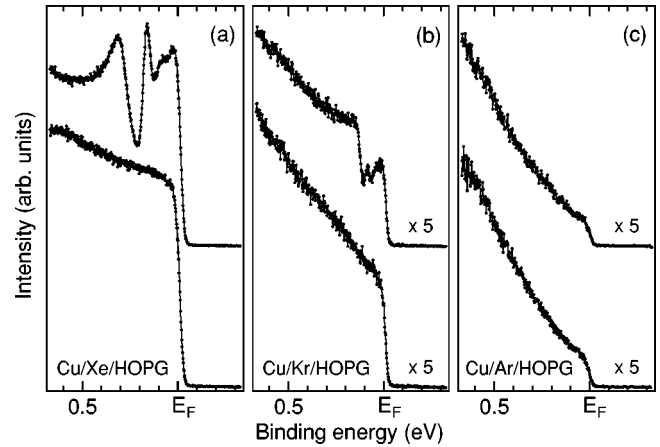


FIG. 4. UPS spectra (He I, normal emission, $T=50$ K) of (a) 1-ML Xe/HOPG (bottom) and after Cu evaporation (top); (b) 1-ML Kr/HOPG (bottom) and after Cu evaporation (top); and (c) 1 ML Ar/HOPG (bottom) and after Cu evaporation (top). The Cu concentration is about 0.05 RG ML. The spectra measured after Cu evaporation have been displaced vertically for clarity. The spectra in (b) and (c) have been multiplied by a factor of 5.

and suggest a much larger WF lowering from the sub-Xe Cu atoms than for the substitutional case. The WF lowerings that we find numerically are comparable to the one expected for alkali adatoms, confirming the results of our WF change measurements. However, because of the well-known tendency of the PWC functional for exaggerating binding energies, the numerical values should not be taken at face value.

Figure 4 shows normal emission UPS spectra in an energy range close to the Fermi level measured for: (a) 1-ML Xe/HOPG (bottom) and after deposition of Cu (top); (b) 1-ML Kr/HOPG (bottom) and after deposition of Cu (top); and (c) 1-ML Ar/HOPG (bottom) and after deposition of Cu (top). The Cu concentration corresponds to 5% of 1 RG ML.

As already found for Xe, Kr and Ar layers likewise induce a folding of the graphite π band. The spectral density measured at the Fermi level is less intense in the two latter cases.² After deposition of 5% of 1 RG ML of Cu the spectra measured for the Cu/Xe/HOPG system present a Fano resonance profile, as shown in Fig. 4(a)(top). After deposition of the same amount of Cu on Kr/HOPG, a less developed resonance profile appears in the UPS spectra [Fig. 4(b)(top)]. Finally, for Cu deposition on Ar/HOPG, no Fano resonance is observed at all [Fig. 4(c)(top)].

In the light of our WF measurements and their analysis within the Topping model these findings are rationalized as follows. The Xe layer fixes isolated Cu atoms and prevents them from diffusing on the surface. Consequently, at low concentrations, the Cu atoms can be treated as single impurities. Every Cu atom contributes to the Fano resonance in photoemission attributed to the interference between the graphite π -band continuum and the discrete Cu $4s$ atomic-like level. For the Cu adatoms on the Ar layer diffusion sets in, leading to the subsequent formation of islands. The concomitant broadening of the Cu $4s$ atomiclike levels into the metallic sp -band is consistent with the absence of a Fano resonance in the UPS spectra: no isolated Cu atoms are

present at the surface. The Cu adatoms on the Kr layer represent an intermediate situation, where already a part of the adsorbed Cu atoms are forming islands. Here only the Cu atoms which remain isolated contribute to the Fano resonance.

Thus our WF measurements confirm that the appearance of the Fano resonance in photoemission is directly linked to the random distribution of isolated Cu atoms on the RG substrate.

IV. SUMMARY

We have studied the WF of Cu/Xe/HOPG as a function of Cu concentration. Our data for the WF change are well described within the Topping model based on a random distribution of isolated Cu impurities on the surface. This analysis

yields high values for the dipole moment p_0 and the polarizability α , indicating that Cu impurities on Xe/HOPG resemble in their outer electronic structure closely alkali impurities on metal surfaces. This finding has been confirmed by DFT calculations.

The geometric information on the arrangement of the Cu impurities on the surface contained in the Topping model and in the theoretical modeling is very important for understanding the appearance of a Fano resonance in photoemission spectra. The presence of isolated Cu impurities at the surface is primordial: it is the atomiclike Cu $4s$ level that interferes with the folded π band of graphite leading to the observed Fano resonance.

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