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Xe and K coadsorption on Ag (110): Observation of a wetting-to-nonwetting phase transition

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The structure of empty electronic levels in Xe on Ag(110) is probed by angle-resolved inverse photoemission. The observed dispersion indicates wetting behavior of a Xe film in (111) orientation on the Ag(110) surface. If the Ag(110) surface is precovered by a metallic potassium layer, the spectra indicate formation of a nonwetting Xe film. The data of the present experiment cast new light on the controversial interpretation of Xe optical spectra and promote the general understanding of wetting and nonwetting adsorption behavior.

Studies of the wetting behavior of various adsorbate-substrate combinations have recently attracted much attention. A detailed understanding of the microscopic processes governing the wetting behavior of adsorbates is tantamount to gaining control over the growth mode of multilayer films, which is of eminent technical importance. A review on recent progress in this area has been published by Bienfait.[1] The general pattern, which emerged mainly from studies on physisorbed films at low temperature, revealed an intimate connection between the wetting behavior and the ratio, R, of the adsorbate-substrate to adsorbate-adsorbate interaction strength. At both low and high values of R usually nonwetting behavior has been observed, whereas complete wetting was hitherto believed to be restricted to a rather narrow intermediate range on the R scale.[1-3] This phenomenon has commonly been referred to as "reentrant nonwetting behavior." There is increasing evidence, however, for the importance of structural effects in wetting phenomena,[1] as illustrated for instance by recent work on wetting behavior of Xe on Pt (111).[4]

The present study reports the observation of a wetting (Frank-van der Merwe growth) to nonwetting (Stranski-Krastanov growth) phase transition for Xe coadsorbed with potassium on a Ag(110) surface. The phase transition has been studied by inverse photoemission spectroscopy (IPE).[5] This is the first example of directly monitoring the effect of a wetting-to-nonwetting phase transition via the unoccupied-level structure.

Figure 1 shows IPE spectra at various angles of incidence obtained after exposure of the Ag(110) surface to 200 L Xe at 50 K (1 L $=10^{-6}$ Torr sec, uncorrected pressure gauge reading). At normal electron incidence four features can be observed in the Xe IPE spectra at about 2.2 eV (A), 3.4 eV (B), 5.0 eV (C), and at 7.6–8.2 eV (D,D').[6] The latter is remarkably broad and is composed of different transitions. This becomes obvious for off-normal electron incidence where feature D is seen to disperse downwards. Features A, C, and D' remain comparatively unaffected by the angular variation. Peak B, however, dominating at normal incidence, shows a dramatic loss in intensity as the angle of incidence is increased to either side. The observed angular dependence of energy positions and intensities indicates the formation of an ordered Xe adsorbate layer. Consequently, the calculated Xe band structure[7] is used for the interpretation of the IPE spectra in the following. Peak B is located 0.6 eV below the vacuum level. It coincides with the bottom of the Xe conduction band.[8,9] The intensity maximum at normal incidence is accordingly assigned to a direct transition at Γ_6^+. The angle-independent emission of peak C is observed at the energy position of the band extrema L_6^+

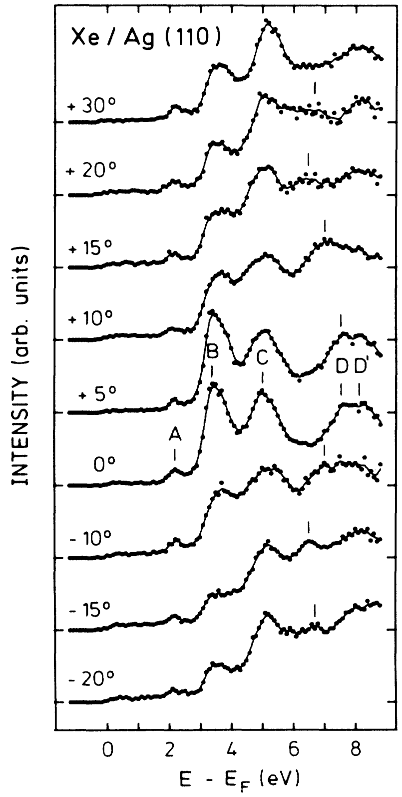

FIG. 1. Inverse photemission spectra of Xe on Ag(110) as a function of the angle of electron incidence.

and X_6^+ and is attributed to density-of-states (DOS) emission from these critical points. Peaks *D* and *D'* coincide at normal incidence with the energy position of the flat bands between Γ_7^+,Γ_8^+ and $L_{4,5}^+,L_6^+$. DOS emission from these bands persists throughout the measured angles and is observed as peak *D'* in all spectra. The downward-dispersing peak *D* is due to direct transitions in the ΓKLU plane of the Xe bulk Brillouin zone. Finally, we turn to peak *A* which is tentatively assigned to a defect state in the band gap 1 eV below the bottom of the conduction band. This assignment will be further substantiated below.

If the work function of the Ag(110) surface is lowered prior to Xe adsorption by predosing it with small amounts of potassium, the shape of the IPE spectra of the bulk Xe layer remains at first unaffected.[8] As the binding energies of the Xe levels are fixed with respect to the vacuum level,[10] the only effect of the potassium-induced work-function change is to shift the spectral features as a whole closer to the Fermi level. This behavior changes dramatically, if the amount of potassium exceeds half a close-packed metallic layer, i.e., for exposures at and beyond the K-induced work-function minimum,[11] where the alkali-metal adsorbate layer character changes from ionic to metallic. First of all, the sticking coefficient and the Xe-substrate binding energy is apparently strongly reduced.[12] More surprising, however, is a radical change in the spectral intensity distribution during the Xe uptake. Figure 2 shows a selection of IPE spectra obtained at various Xe coverages on Ag(110) +2 ML K (one monolayer = 1 ML) ranging from zero to about 1000 L Xe at 7×10^{-6} Pa Xe background nd pressure. During uptake of the first 2–3 Xe layers [spectra (b)–(d)] the spectra are qualitatively similar to the Xe bulk spectra on the bare Ag(110) surface apart from the work-function-related shift. For higher Xe exposures [spectrum (e)] peaks *A* and *B* take the lead in the intensity accretion leaving peak *C* as a secondary feature, finally appearing only as a high-energy shoulder of peak *B*. Peaks *D* and *D'* eventually disappear as the Xe layer thickens.

Figure 3 shows IPE spectra at various angles of incidence from a thick Xe layer on Ag(110) +2 ML K. Apart from marginal changes in relative intensity, the spectra are angle independent.

The similarity of the IPE spectra from the very first Xe layers on the potassium-covered Ag surface [Figs. 2(c) and 2(d)] with the IPE spectra presented in Fig. 1 indicates that the Xe layer initially grows in the same mode as on the bare Ag(110) surface. After completion of the first two to three layers, however, a striking change occurs leaving the bulk Xe in a different, obviously disordered state. As the triple-point temperature, T_t, of Xe lies much higher [for bulk Xe at 161.4 K; for a two-dimensional Xe layer on graphite at 100 K (Ref. 13)] this disordered phase must be solid. A roughening transition can be excluded, because it is substrate independent and occurs at

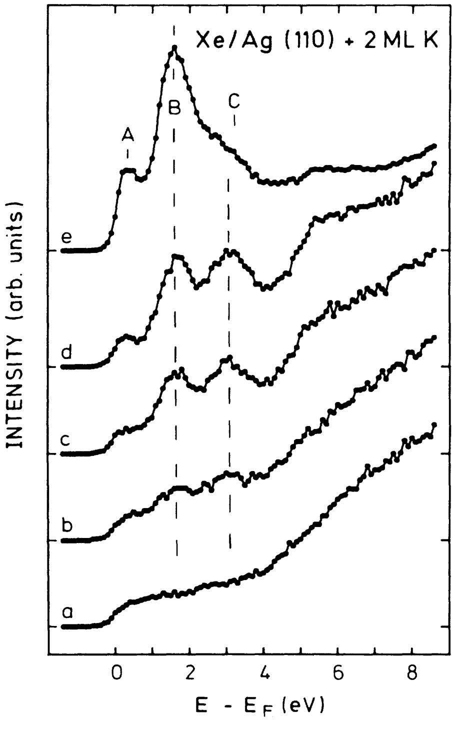

FIG. 2. Inverse photoemission spectra of Xe on Ag(110) + 2 ML K as a function of coverage: (a) 0 L Xe; (b) 270 L Xe; (c) 320 L Xe; (d) 380 L Xe; (e) 1000 L Xe at 7×10^{-6} Pa Xe background pressure.

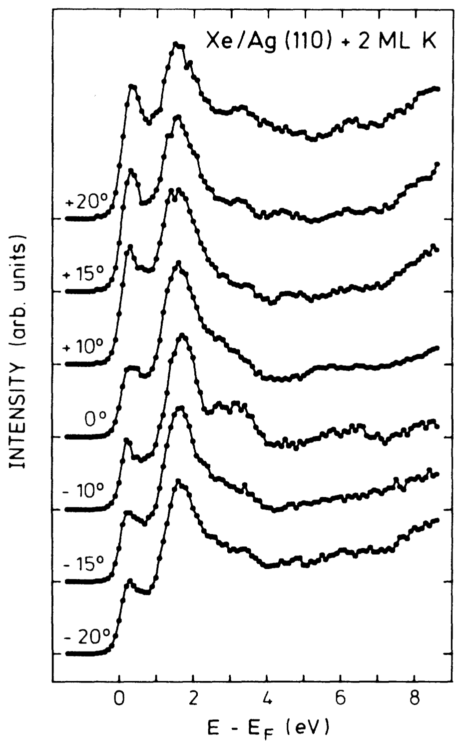

FIG. 3. Inverse photoemission spectra for 1000 L Xe on Ag(110) + 2 ML K at 7×10^{-6} Pa Xe background pressure as a function of the angle of electron incidence.

about $0.8T_t$.[14] The only phase transition then which can account for the present results is a wetting-to-nonwetting transition. As pointed out at the beginning, such a transition is expected to occur if the adsorbate-substrate interaction is reduced below a critical value which is achieved in this experiment by K "intercalation." Furthermore, it is characteristic for nonwetting behavior that the first few layers may grow layer by layer before enough stress is accumulated to cause the film to break apart.[1,15] This is just what we observe here as illustrated by the spectra in Fig. 2. Finally, the rupture of the larger Xe domains with Xe bulk band structure into small clusters with different, probably more atomiclike electronic structure, accounts very well for the spectral changes observed in the present case. Electron-energy-loss spectroscopy (EELS) results on gas-phase Xe (Ref. 16) may serve to interpret the spectra, although no direct comparison between EELS and IPE spectra is possible[17] because the final states are vastly different. However, the energy spread between the lowest Xe $5p^5 6s$ and the highest Xe $5p^5 5d$ atomic excited state may yield a rough estimate of the energy separation between $6s$ and $5d$ states in IPE. This energy spread amounts to ~ 2 eV (Ref. 16) which correlates nicely with the combined width of features *B* and *C* in the IPE spectra of Fig. 3. Drawing further on this analogy we assign peak *B* to the Xe $6s$ level which is entirely consistent with the Γ_6^+ assignment of the corresponding peak in the wetting Xe film of Fig. 1. Peak *C* contains the Xe $6p$ and $5d$ atomic levels which in the wetting film are spread out over several eV in the *p*- and *d*-derived energy bands (peaks *C*,*D*,*D'*). Peak *A* is still left for discussion. In a previous study[8] it was observed that the intensity of feature *A* is not well reproducible. This was taken to be characteristic of an impurity-induced level. The present study revealed, however, that nonwetting behavior of the Xe film is always associated with a larger intensity of peak *A*. Apparently the intensity of peak *A* is inversely related to the Xe domain size. This suggests an assignment of peak *A* to surface or interface states on Xe crystallites (grain boundaries). Such an identification is supported by recent thermal desorption data for Xe from Ag(111),[18] which showed that a considerable fraction of Xe atoms in the first and second monolayer is positioned at the perimeter of small islands even if the adsorbed Xe film grows layer by layer. The nonwetting transition reduces the domain size and therefore increases the intensity of the defect-induced peak *A*.

Considering the position of peak *A* directly at the Fermi level in the nonwetting films studied here it is tempting to associate the wetting-to-nonwetting phase transition with the population of this defect state by substrate electrons. However, an IPE spectrum characteristic of a nonwetting film was also observed for bulk Xe on Ru(001) (Ref. 17) and there peak *A* is located about 3.5 eV above E_F. Consequently, population of the interface or surface states related to peak *A* is not a necessary prerequisite for nonwetting behavior.

Nonwetting behavior of Xe on K has already been conjectured by Onellion and Erskine[19] on the basis of a recent ultraviolet photoemission spectroscopy (UPS) study of Xe and K coadsorption on Ni(110) (Ref. 20) which corroborates our conclusions. In view of the considerable corrugation of the Ag(110) surface and the 7% mismatch between the distance of neighboring rows on the Xe(111) plane and neighboring grooves in the Ag(110) surface, the wetting behavior of the Xe film on the bare silver surface may seem surprising. However, a higher-order commensurability similar to Xe on Pt(111) (Ref. 4) is possible in the present case as well. On Ag(111) wetting behavior is observed at least up to four layers.[18] On Cu(110) a recent low-energy electron diffraction (LEED) study reports the formation of a complete first monolayer with exactly the Xe-Xe bulk spacing. The stress imposed by the corrugation is already released in the second layer which exactly reproduces the hexagonal structure of bulk Xe (Ref. 21). Under such conditions wetting behavior is expected up to infinite thickness because no stress is accumulated any more. Thus we conclude that the wetting behavior of Xe on Ag(110) is nothing very peculiar.

Recently, two entirely different IPE spectra of bulk Xe films on Au(110) and Ru(001), respectively, have been published by two different groups.[17,22] No account was given for the difference. The present study resolves the enigma. The Xe IPE spectrum of Xe on Au(110) (Ref. 22) indicates wetting behavior, whereas Xe on Ru(001) shows the IPE spectrum characteristic of a nonwetting film. As a layer-by-layer growth of Xe on Ru(001) has been demonstrated by UPS for at least two layers[12] this indicates that the film rupture occurs only after stress has been accumulated in three or even more monolayers. Of course the limiting thickness will depend on temperature. The Xe-Ru interaction is slightly stronger than the Xe-Ag interaction [0.25 eV for Ru(001) (Ref. 12) versus 0.22 eV for Ag(111) (Ref. 18)]. This seems to fit into the general pattern of reentrant wetting behavior, but the difference of the interaction energies is rather small and structural relationships are likely to be of more importance in this case.

The wetting behavior of Xe reported here delivers an alternative and explanation for the so-called "optical switching" observed in various rare-gas–metal adsorption systems.[23] Flynn and co-workers realized that the excitonic peak characteristic for bulk rare-gas optical spectra persists for rare-gas adsorption on low-work-function metals (e.g., Mg, alkali metals) even at submonolayer coverages, whereas for rare-gas–metal systems where the metal has a larger work function (e.g., transition metals) it disappears in the low-coverage limit. They provided an explanation in terms of an ionic versus neutral excited state depending on the ratio of the excited-state ionization energy to the substrate work function. This explanation was rejected by Lang *et al.*[24] but later on was refined[25] and backed up by a more elaborate theory.[26] However, a reexamination of the two different classes of rare-gas–metal adsorption systems reveals that they are most probably characterized by their wetting behavior. Nieuwenhuys, van Aardenne, and Sachtler[27] observed a correlation between the Xe-induced work-function change and the Xe-substrate binding energy. By the same token, the low-work-function metals, where Xe induces only a small work-function change, are also "weak" substrates, on which nonwetting behavior has to be expected.[1] In wetting systems (e.g., Xe on Au, Al, Ti) the film becomes very thin in the low-coverage limit and the excitonic peak disappears due to substrate-mediated screening. In nonwetting systems (e.g., rare gases on alkali metals, Xe on Mg, Ar and Kr on Al) clusters are formed also at low coverage which enable the excitonic peak to persist even for small amounts of adsorbed gas. Evidently, the average dipole moment per rare-gas atom is also much smaller in the latter case.

In summary, we report the observation of a wetting to nonwetting phase transition for Xe films on a Ag(110) surface predosed with potassium. The transition occurs as the potassium surface concentration exceeds half a monolayer and is accompanied by profound changes in the structure of unoccupied electronic levels. The results are consistent with theoretical models of nonwetting behavior on weak substrates and recent photoemission results for Xe + K on Ni(110). The observed phase transition could provide a simple explanation for the long-standing controversy on the "optical switching" in rare-gas layers. The study also demonstrates the potential of inverse photemission spectroscopy for monitoring structural changes in general.

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