Two-dimensional condensation of potassium on Ag(001)

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Temperature- and coverage-dependent soft-x-ray photoemission and photoabsorption studies on potassium-covered Ag(001) surfaces demonstrate the formation of potassium two-dimensional compressed islands, even at coverages far below saturation. The expected disperse-overlayer structure is metastable, and is irreversibly transformed into the compressed phase at higher temperature. These results indicate that the short-range attractive adsorbate-adsorbate interaction overcomes the electrostatic repulsion and the surface-corrugation potential, and that the adsorbate-substrate charge transfer is insignificant, supporting recent theoretical studies.

The chemisorption of alkali-metal atoms on metal substrates attracts large interest in light of various competing physical mechanisms determining the bonding of the alkali-metal overlayer. Important aspects of these systems are the nature of the adsorbate-adsorbate interaction, the amount of charge transfer between adsorbate and substrate, and the magnitude and symmetry of the surface-corrugation potential.[1,2] Experimental results on alkali-metal adsorbate-induced work-function changes,[2,3] thermal desorption of alkali-metal ions,[4] and the formation of disperse ordered overlayers at alkali-metal coverages below saturation[1,2] have all contributed to the formulation of a widely accepted charge-transfer model. Here, the observed alkali-metal overlayer properties are dictated by a large coverage-dependent charge transfer from the adsorbate to the substrate, responsible for the creation of a strong electrostatic repulsion among adsorbates.[5] Recent calculations suggest, however, that such charge transfer is negligible at all coverages, and that the properties of these systems are due to the surface dipole field resulting from the charge distribution of the adsorbate-substrate chemical bond.[6,7]

In this Rapid Communication, using temperature- and coverage-dependent high-resolution x-ray photoemission spectroscopy (XPS) and x-ray photoabsorption spectroscopy (XAS), we report that below the saturation coverage the stable phase of a potassium overlayer on Ag(001) consists of dense potassium-potassium *attraction*-dominated *two*-dimensional islands. The expected potassium-potassium *repulsion*-dominated phase is only obtained by depositing alkali-metal atoms at a substrate temperature of 90 K, and it is irreversibly transformed into the high-density phase by temperature annealing. The presence of a stable condensed phase and of an activation barrier are related to the total energy of the system, in which the short-range potassium-potassium attractive interaction competes with the long-range electrostatic repulsion between adsorbates and with the surface corrugation poten-

tial. These observations indicate that the charge transfer between adsorbate and substrate is insignificant, and suggest that the surface corrugation potential plays an important role in the alkali-metal condensation process.

High-resolution photoemission and photoabsorption spectra were measured using the AT&T Bell Laboratories Dragon high-resolution soft-x-ray beamline[8] located at the National Synchrotron Light Source. In the photoemission spectra, the total-energy resolution was set at 200-meV full width at half maximum (FWHM) for the K 2p, and 150-meV FWHM for the Ag 3d core levels. In the K $L_{2,3}$ photoabsorption spectra the resolution was set at 150-meV FWHM. The Ag(001) sample was cleaned by Ne$^+$ sputtering and 800-K annealing cycles. The residual gas pressure was less than 5×10^{-10} torr during the alkali-metal atoms evaporation (SAES getters), and 5×10^{-11} torr during the data acquisition. For the spectra shown here, no C and O contaminations were detected by XPS with a sensitivity of 0.02 and 0.05 monolayers (ML), respectively. The potassium coverage was measured from the integrated intensity of the K $2p_{3/2}$ XPS peak normalized to the background. The peak intensity corresponding to the complete potassium first layer was determined by monitoring the appearance of the second-layer peak at 0.7-eV-lower binding energy in the K 2p XPS spectrum. The first-layer saturation coverage of samples prepared and held at 90 K is determined to be 0.5 ML, by the observation of a sharp $c(2 \times 2)$ low-energy-electron-diffraction (LEED) pattern.

Figure 1(a) shows the coverage dependence of the K 2p XPS spectra taken on surfaces prepared and held at 90 K. Both spin-orbit-split XPS peaks are observed to shift monotonically with coverage for a total amount of 0.7 eV. This dependence, similar to that observed for potassium on Ni(001),[9] Ru(001),[10] and Pt(111),[11] is characteristic of a disperse adsorbate phase, where, at each coverage, the long-range electrostatic repulsion keeps the alkali-metal atoms away from each other. Consequently, the
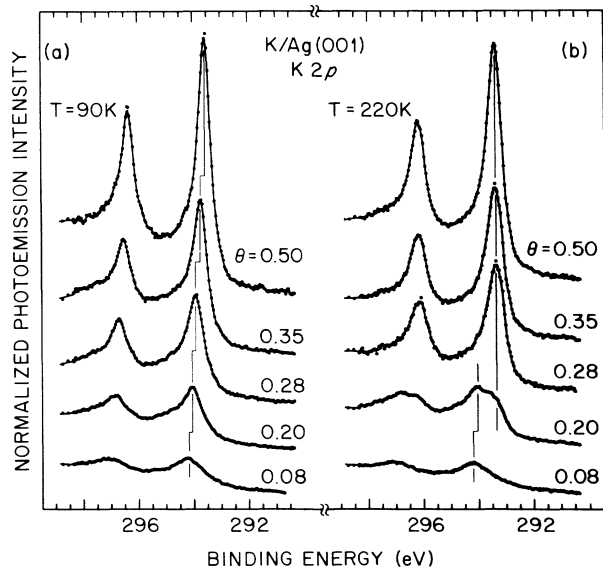
FIG. 1. Temperature- and coverage-dependent K $2p$ XPS spectra of potassium-covered Ag(001) surfaces. The spectra are normalized to the background, and taken with 360-eV photons. (a) Samples prepared and measured at 90 K. (b) Samples prepared and measured at 220 K.
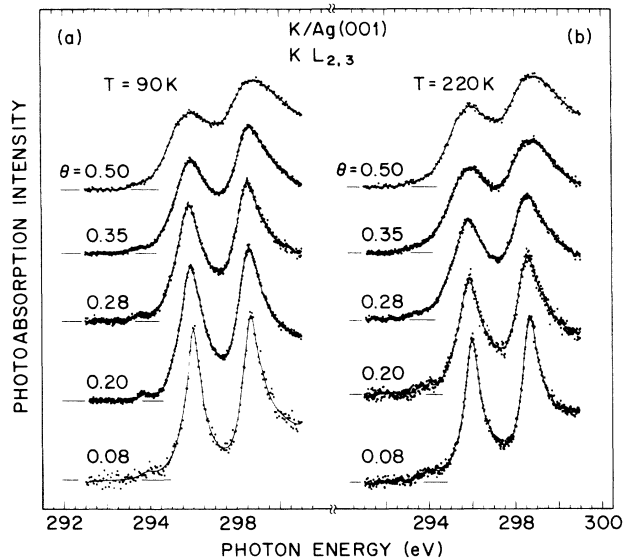

FIG. 2. Temperature- and coverage-dependent K $L_{2,3}$ XAS spectra of potassium-covered Ag(001) surfaces. The spectra are normalized to their respective area, and measured monitoring the K LVV elastic Auger yield. (a) Samples prepared and measured at 90 K. (b) Samples prepared and measured at 220 K. The changes in the peak width can be easily visualized by the peak height with respect to the background (horizontal lines).

photoemission binding energy decreases with increasing coverage as a result of larger electron density in the core region,[7,9,10] and better core-level screening. The absence of chemically shifted surface components in our Ag $3d$ XPS spectra indicates, however, that there is not a large adsorbate-substrate charge transfer. For all of the K/Ag(001) surfaces that we have studied, the measured Ag $3d$ spectra have width and energy position very similar to those of the clean Ag(001) surface, within 0.05 and 0.1 eV, respectively.[12] This observation, supporting recent theoretical calculations, shows that it is the charge-redistribution and not the charge transfer which determines the coverage-dependent properties of alkali-metal-substrate chemisorption systems, and that the electrostatic repulsion between adsorbates is due to the dipole field of the polarized adsorbate-substrate bond.[6,7]

The formation of this repulsion-dominated disperse phase is further confirmed by the photoabsorption spectra shown in Fig. 2(a). These spectra are dominated by the K $2p^{-1}3d$ transition. The low-coverage data show two sharp $2p^{-1}3d$ spin-orbit-split excitation peaks that get significantly broader as the coverage is increased. This behavior nicely indicates the transition from isolated potassium atoms to the formation of K−K bonds, where the broadening of the $2p^{-1}3d$ excitations are induced by the overlap between $3d$ orbitals of adjacent potassium atoms and the formation of $3d$ bands.

Below 0.25 ML coverage, the LEED pattern exhibits rings of increasing radius with increasing potassium coverage. Further coverage increase to 0.25, 0.33, and 0.5 ML give $c(4\times2)$, (3×2), and $c(2\times2)$ patterns, respectively.[13] The K−K distance at the overlayer saturation coverage is 4.08 Å (the Ag lattice parameter), a value ~10% smaller than in the bulk (4.51 Å at 90 K). These LEED patterns indicate that the adsorbate overlayer is al-

ways commensurate with the substrate. The absence of an incommensurate pattern with hexagonal symmetry and lattice parameter varying with adsorbate coverage, as expected for a uniformly spaced adsorbate overlayer, provides strong evidence for preferred adsorption sites for the alkali-metal atoms. This suggests that while the long-range electrostatic repulsion is responsible for the disperse phase, the substrate corrugation potential ensures the overlayer being commensurate with the Ag(001) surface and prevents the disperse phase from being uniformly spaced.

We now discuss the changes of the XPS and XAS spectra upon temperature annealings. Figure 1(b) shows the coverage dependence of the K $2p$ XPS spectra taken on surfaces prepared and held at 220 K. Above 0.08 ML, an extra peak appears at a binding energy of 293.5 eV and gains intensity with increasing coverage. In contrast to the monotonic energy shift observed in Fig. 1(a), the binding energy of this peak is almost independent of coverage, and is slightly lower than that of the 90-K sample with 0.5-ML coverage shown in Fig. 1(a). The K $2p_{3/2}$ binding energies of various samples prepared at 90 and 220 K are summarized in Fig. 3. Spectra very similar to those shown in Fig. 1(b) were obtained on samples with the same coverages but prepared at 90 K and then annealed to 220 K. Moreover, the XPS spectrum remained unchanged after a sample was prepared or annealed at 220 K and then cooled back down to 90 K. In short, the process leading to the appearance of the new lower binding-energy peak after the 220 K annealing is irreversible. The overlayer saturation coverage for the samples prepared at 220 K is ~10% higher (0.55 ML) than for those prepared and held at 90 K (0.5 ML, see Fig. 3).[12]
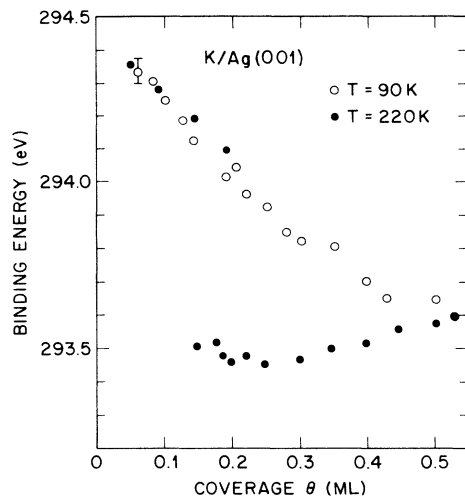
FIG. 3. Summary of the binding energy of the K $2p_{3/2}$ spin-orbit-split component as a function of coverage θ. Open circles refer to samples prepared and measured at 90 K, filled circles to samples prepared and measured at 220 K. The error bar of 80 meV is indicated on one of the experimental points.

The surprising nearly constant K $2p_{3/2}$ binding energy in samples with different coverages and annealed at 220 K, and its similarity to that in the 90 K $c(2\times2)$ overlayer sample, indicates that stable potassium islands with compressed K—K bonds are formed even at coverages far below saturation. The temperature annealing, required for the formation of this new condensed phase, shows the existence of an activation barrier, which is overcome by the increased surface mobility of the adsorbates.

The interpretation of the photoemission data is in agreement with their corresponding photoabsorption spectra shown in Fig. 2(b). We observe that the $2p^{-1}3d$ excitation peaks in surfaces with potassium coverage above 0.2 ML are broader than those with the same coverage in the disperse phase [compare the top three spectra of Figs. 2(a) and 2(b)]. Concurrently with the nearly constant photoemission binding energy discussed above, the widths of the photoabsorption peaks do not change appreciably at coverages above 0.20 ML. This extra broadening, reflecting the $3d$-band formation at coverages far below saturation, further supports the formation of islands by the potassium atoms.

Based on the photoemission data, we estimate that, for samples annealed to 220 K and with coverages greater than 0.25 ML, more than 90% of the adatoms are in the condensed phase. The two-dimensional nature of the potassium islands is supported by the observation of a single spin-orbit doublet in the K $2p$ XPS spectra, and of a single desorption temperature.[14]

Additional evidence for the formation of a high-density potassium phase comes from our LEED studies.[12] All surfaces annealed at 220 K no longer have the disperse phase LEED patterns, but show a (1×1) pattern with a background that increases with coverage.[15] However, after annealing at ~400 K, $(5\times n)$ LEED patterns, with $n=4$ at saturation coverage and $n=10$ below saturation, are observed when cooling the samples back down to 220

K. This 400-K annealing does not cause significant changes in the XPS and XAS spectra. In contrast to the disperse phase, the appearance of these LEED patterns after the 400-K annealing testifies to the formation of potassium islands with the same structure at any coverages. Moreover, these $(5\times n)$ LEED patterns and the observation of a higher saturation coverage in the condensed phase (0.55 ML) than in the low-temperature disperse phase (0.5 ML), suggest that the structure of the commensurate condensed islands is *quasihexagonal* with an average K—K bond distance of 4.15 Å.[16] This structure is very similar to that expected for a free-standing potassium single layer.[17]

Adsorption studies of Na and Cs on this Ag(001) surface show a very similar behavior to that of potassium: a metastable dispersed overlayer at low temperatures, and a phase transition into a stable condensed layer at coverages below saturation.[12] The saturation coverages and the LEED patterns of the Na and Cs condensed phases, however, are different from those of K, supporting the fact that the observed phase transition is not due to a substrate surface reconstruction.[12]

This alkali-metal condensation process is most surprising when compared to all previous reports on the chemisorption of alkali-metal atoms on metal surfaces. The absence of experimental observation of alkali-metal condensation, in fact, strongly supported the charge-transfer model.[1,2] A condensed alkali-metal phase has been suggested from LEED studies for K on Cu(001) at coverages close to alkali-metal overlayer saturation,[18] and for K and Cs adsorbed on graphite.[19]

The unexpected condensation in the Ag(001)-K system, and why it was not observed in alkali-metal adsorption on other substrates, except graphite and Cu(001), suggest two criterions responsible for the alkali-metal condensation on metal surfaces. They are (1) the total energy decrease for the formation of alkali-metal–alkali-metal bonds in the islands must be greater than the increase due to the electrostatic repulsion among adsorbates and the substrate corrugation potential, and (2) the temperature needed to overcome the activation barrier caused by the electrostatic repulsion and the substrate corrugation potential should be lower than the dissociation temperature of the condensed alkali-metal islands. Since the adsorbate dipole moment decreases appreciably with the decreasing average separation among alkali-metal adsorbates,[3,7] the condensation process is primarily dictated by the competition between the alkali-metal–alkali-metal attractive interaction and the substrate surface corrugation potential. According to these ideas, in graphite, because of the small surface corrugation potential, the alkali-metal atoms form condensed islands with a very small activation barrier (80 to 130 K annealings).[19] In the case of the K/Ag(001) system, and similarly for the K/Cu(001) system, although the weak corrugation potential still makes the condensed phase more stable than the disperse one, the condensation requires a larger surface mobility, i.e., a higher temperature to overcome the activation barrier. Finally, the absence of alkali-metal condensation on many other metal surfaces can be attributed to larger substrate corrugation potentials.

In conclusion, we have reported the formation of a stable high-density phase in the K/Ag(001) adsorbate system. This phase is characterized by a strong short-range attractive K-K interaction and by a compressed K-K bond distance. Our observations indicate that the charge transfer between adsorbate and substrate is insignificant, in agreement with recent theoretical works.[6,7] The stability of the condensed phase and the presence of an activation barrier are related to the K-K short-range attractive interaction, the long-range electrostatic repulsion, and the effect of the surface corrugation potential. We suggest that alkali-metal condensation will occur on substrates with low corrugation potential and can be further favored on surfaces quasicommensurate with the *hexagonal* structure of the alkali-metal *two*-dimensional layer.

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