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Ag deposition onto Xe: Clustering, incorporation, and surface attraction

T. R. Ohno, J. C. Patrin, U. S. Ayyala, and J. H. Weaver
Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

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Processes associated with Ag-atom deposition on condensed layers of Xe have been investigated using high-resolution x-ray photoemission. Depositions of small amounts of Ag produce distinct signatures that correspond to metallic clusters on the Xe layer and isolated atoms or small clusters embedded in the Xe film. The binding energy of the latter is dependent on the Xe thickness because of substrate-mediated differences in core-hole screening. Time-dependent studies show that Ag clusters formed on the surface are attracted to the surface via van der Waals forces, sinking in the Xe layer with rates that are dependent on temperature.

It has been shown that multilayers of solid Xe act as noninteracting substrates on which clusters can be formed, even at low temperature.[1,2] Several studies have used this tendency to cluster to produce aggregates of metals and semiconductors and to bring them into contact with various substrates following the sublimation of the Xe buffer layer. Such cluster-assembled overlayers on semiconductors and high-temperature superconductors, for example, have shown greatly suppressed reactivity. This can be understood because atom-substrate interactions are replaced by cluster-substrate interactions.[1,2] Transmission-electron-microscopy (TEM) studies of the distribution of such clusters on silica have shown isolated clusters when the amount of material deposited on Xe was less than ~5 Å. Evidence of increased connectivity of aggregates on the surface was found for higher deposition. These studies notwithstanding, one can only infer the spatial and size distribution of clusters on the buffer layer.

This paper focuses on issues related to atom deposition on solid Xe buffer layers on GaAs(110). In addition to cluster formation on the surface, we observe Ag implantation in the Xe layer that reflects the energy distribution of the impinging Ag atoms. We show that the Ag clusters are attracted to the GaAs substrates by van der Waals force. They are drawn to the substrate with a rate that is dependent on temperature. To our knowledge, these are the first studies to demonstrate implantation and surface attraction. Changes in the Xe and Ag photoemission spectra also provide insight into the nature of the core-hole screening.

High-resolution x-ray photoemission results were obtained with a spectrometer described in detail elsewhere.[3] A monochromatized Al $K\alpha$ x-ray beam was focused to a 300-μm spot, and the photoemitted electrons were energy analyzed with a hemispherical analyzer and a position sensitive resistive anode. The energy resolution was 0.7 eV at a pass energy of 50 eV. The temperature could be varied between ~20 and ~350 K using a closed-cycle He refrigerator and a compensating heater.[4] For most experiments discussed here, the substrates were n-type GaAs cleaved *in situ* to form mirrorlike (110) faces. For some experiments, Cu substrates were prepared by mechanical polishing and Ar^+ sputtering. The substrates were cooled to 25 K and were then exposed to high purity Xe for times known to produce definite thicknesses of Xe.[1,5,6] Silver was evaporated from heated Ta boats, and the amount was measured using a quartz microbalance. Deposition rates were typically 0.5 Å/min, where 1 Å corresponds to 5.9×10^{14} atoms/cm^2. The system pressure was less than 4×10^{-10} Torr during deposition; operating pressures were $\sim5\times10^{-11}$ Torr.

Figure 1 shows normalized core-level energy distribution curves, EDC's, for Ag depositions ranging from 0.12 to 3 Å onto ~50-Å-thick Xe layers on GaAs. These Ag depositions were done at 50 K and the measurements were made at that temperature. The Ag $3d_{5/2}$ emission could be represented by a single symmetric feature, labeled A, for 3 Å Ag on Xe and the valence bands were characteristic of the bulk metal, based on the width of the $4d$-derived bands. Line-shape analysis for the Ag $3d_{5/2}$ emission for 3 Å deposition showed a full width at half maximum (FWHM) that was broader than that of bulk Ag, namely, 1.1 eV compared to 0.8 eV. When the amount of Ag was smaller, a second $3d_{5/2}$ feature at higher binding energy was clearly distinguishable, labeled B. Feature B probably accounts for the broadening at higher coverage but it could not be resolved. The spin-orbit companion of feature B was also observed while no evidence of contaminants was seen in a wide scan, indicating the feature is not a chemically shifted component. Figure 1 shows that both Ag $3d_{5/2}$ features shifted to higher binding energy with reduced total Ag deposition, but the separation between them increased and their presence was more evident at low coverage.

Peak A in Fig. 1 arises from Ag clusters on the Xe surface.[1,2] Although the diffusion coefficient is not known for Ag on Xe, the experimental results indicate that diffusion is favorable. Moreover, surface motion is assisted by energies associated with Ag-atom condensation and Ag—Ag bond formation. We note that TEM images for Au clusters grown on Xe and then deposited onto silica showed that the nucleation density was $\sim10^{12}$ clusters/cm^2 for nominal deposition of 1 to 10 Å. For depositions of ~1 Å, the cluster distribution exhibited a maxima at ~10-Å radius and few were observed with radii below ~5 Å. We infer a similar distribution for Ag growth.

Comparison of the binding energy of feature *A* for 3 Å Ag deposition on Xe and for a 100-Å Ag film shows a shift of 1 eV to higher binding energy for the cluster. This is due in part to the energy reference of the Xe buffer layer because the vacuum level of Xe aligns with the vacuum level of the substrate.[5-7] Subsequent cluster formation on Xe produces a common vacuum level for the cluster and the Xe. Indeed, the binding energy for feature *A* for equal Ag coverages on Xe on GaAs and on Cu differed by an amount equal to the difference in substrate work functions.

The results of Fig. 1 show that feature *A* shifted to greater binding energy as the amount of Ag deposited on Xe was decreased. This is consistent with results for metal cluster growth on amorphous carbon for depositions greater than $\sim 10^{14}$ atoms/cm^2 (Refs. 8 and 9). Wertheim and DiCenzo[8] proposed that the shift was caused by an unneutralized charge on the cluster that can be screened only by cluster electrons. In this case, the apparent core-level binding energies for atoms in clusters would vary inversely as the cluster radius R. Our results show a 0.8-eV shift of feature *A* relative to bulk Ag for 0.5 Å Ag deposition on Xe, with corrections for the energy level references. Assuming a $1/R$ dependence for spherical clusters, this would suggest the growth of clusters with a 9-Å radius and containing ~150 atoms. This cluster size and associated nucleation density agree very well with the TEM results and estimates from photoemission intensities.[1] Results for lower deposition of Ag showed shifts that were consistent with decreasing cluster size and approximately constant nucleation density.

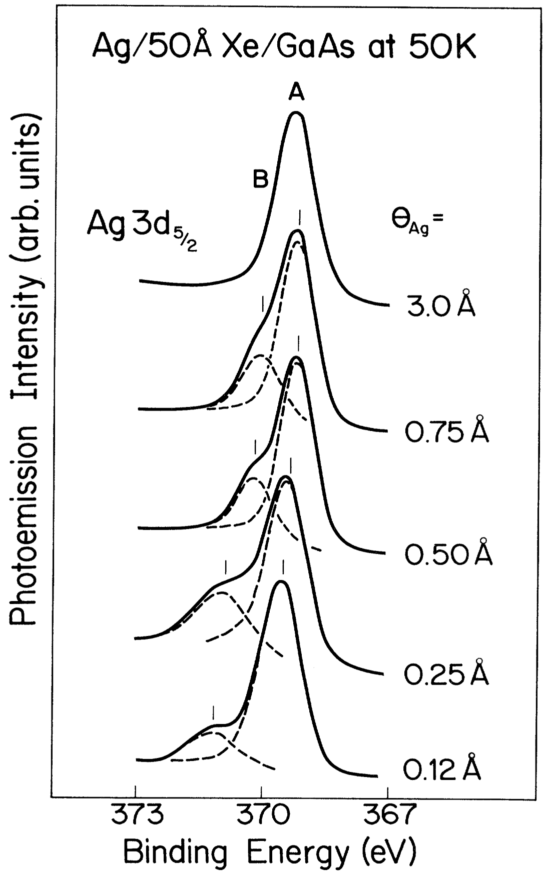

FIG. 1. Ag $3d_{5/2}$ core-level EDC's for different amounts of Ag deposited on 50 Å of Xe on *n*-type GaAs at 50 K. Peak *A* is due to clusters formed on the surface and peak *B* is due to atoms implanted and then trapped in the Xe. Peak *A* shifts to higher binding energy as smaller clusters are formed on the surface. The position of peak *B* approaches that of isolated atoms at a nominal deposition of 0.12 Å. Changes in the binding energy of peak *B* result from coalescence of the implanted Ag atoms.

The results of Fig. 1 show a second feature, labeled *B*, that results from the penetration of a fraction of the impinging Ag atoms and their subsequent matrix isolation. Such penetration reflects the dynamics of Ag-atom impact. In particular, the mean kinetic energy of Ag atoms from a 1300-K source is ~0.17 eV, their distribution in energy follows Maxwell-Boltzmann statistics, and ~10% have energies of above 0.45 eV. These impact energies exceed the bulk cohesive energy of Xe, namely, 0.17 eV per atom.[10] Once incorporated, the atoms are trapped because bulk diffusion in solid Xe is small.[11] [Cu diffusion in Kr at 35 K is characterized by a diffusion constant of 4×10^{-15} cm^2/s (Ref. 12); the numbers are not known for Ag diffusion through Xe at 50 K.] Support for this conclusion comes from photoadsorption studies of Ag and Xe condensed at $T \leq 38$ K where matrix isolation was achieved when the Xe- to Ag-atom ratio exceeded ~100 (Ref. 13). If we assume that the implanted Ag atoms are distributed within a few layers of the surface, then the ratio of Xe to Ag would be ~100 for 0.12 Å Ag, suggesting that the Ag atoms could be isolated.

The spectroscopic results for feature *B* for low coverage are also consistent with Ag atom isolation since the binding energy is close to that of free atoms (discussed below). The results of Fig. 1 also show that the linewidth and binding energy of feature *B* changed as the amount of Ag increased. In the coverage range from 0.12 to 0.25 Å, there was relatively little change in energy but feature *B* broadened. We speculate that the broadening was due to the coexistence of isolated atoms and small clusters. The formation of such aggregates in the near-surface region of Xe becomes increasingly likely as the density of embedded atoms increases. The measured binding energy of a photoelectron from the aggregate then depends on the coordination number of the emitting atom because extra-atomic screening of the core hole occurs by charge transfer from adjacent atoms.[14] (The intensity of feature *B* also increased from 13% to 20% of the Ag intensity between 0.12- and 0.25-Å deposition, but intensity ratios should be viewed with caution since the emission from trapped Ag would be attenuated by the Xe matrix and the emission from Ag atoms in clusters would be attenuated by the clusters themselves.)

Core-hole screening for Ag atoms trapped in a sufficiently thick Xe layer reflects the polarization of the

Xe matrix. In this case, the energy of peak *B* can be compared with the energy of an isolated Ag atom. Johansson and Mårtensson[15] have calculated an energy difference of 7.7 eV for the measured binding energy of the core levels in Ag metal and in Ag atoms where the energy reference for the metal was the Fermi level E_F, and that for the atom was the vacuum level.[16] Thus the Ag $3d_{5/2}$ binding energy for a free atom is 375.9 eV referenced to the vacuum. For a Ag atom in Xe on *n*-type GaAs, the vacuum level is determined by the affinity of GaAs, namely 4.1 eV. The Ag $3d_{5/2}$ energy of an atom with respect to E_F is then 371.8 eV. Incorporation within the polarizable Xe medium would introduce a shift to 370.8 eV based on results for Pd atoms in Xe.[16] This value agrees quite well with the measured binding energy of peak *B*, namely, 371.1±0.1 eV for 0.12 Å Ag on 50 Å Xe, supporting the interpretation that feature *B* arises from matrix-isolated Ag atoms in Xe.

The above discussion has assumed that there were no substrate contributions to screening of core holes excited in Ag atoms and clusters. In Fig. 2 we show results obtained as a function of Xe thickness that sought to identify effects related to substrate-mediated effects. In each case, the amount of deposited Ag was 0.5 Å and the results were normalized to peak height. Although there was no appreciable dependence of the total Ag $3d_{5/2}$ emission on the Xe thickness, the energy offset of feature *B* relative to feature *A* increased with increasing thickness. The measured energies of *A* and *B* are summarized in the inset of Fig. 2 for Xe layer thicknesses of 15–75 Å. The invariance of feature *A* is consistent with its metallic character[17] while the changes in feature *B* reflect the creation of an image charge by photoionization. In this case, a positive charge is assumed to be created on the outer Xe plane such that the local potential is altered by the resulting electrostatic fields, causing an apparent shift in binding energy.[5,18] We have calculated the dependence of this image charge-induced shift on the layer thickness, yielding the solid line shown in the inset of Fig. 2. The absolute binding energy for the calculated results has been shifted by 0.5 eV to facilitate comparison with experiment. The good agreement shown could probably be improved by recognizing that the photoionized Ag atoms are distributed in the Xe layer and that the distance between the ion and its image is overestimated. We also suspect that a similar study for very low Ag coverages would yield positions for *B* that are more representative of ionized isolated atoms than those of Fig. 2 for 0.5 Å.

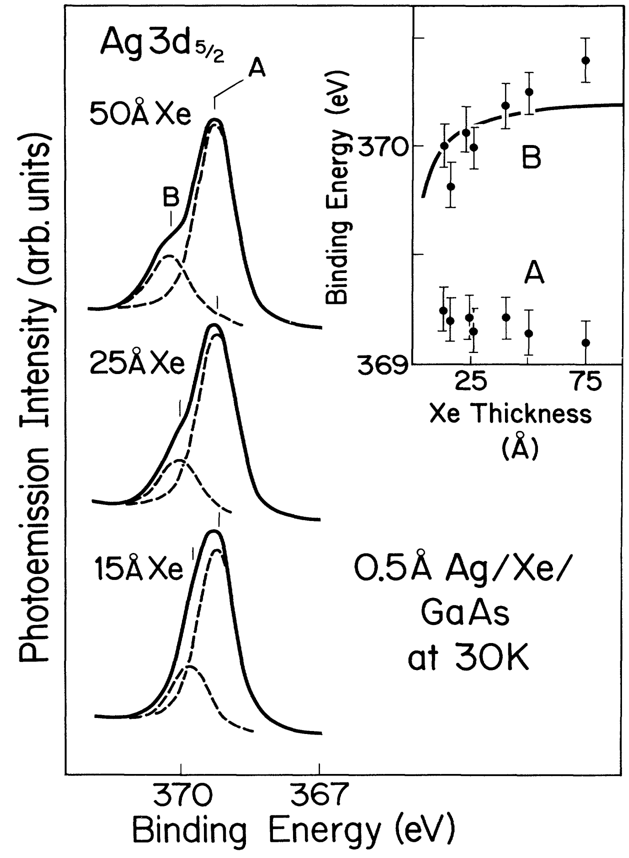

FIG. 2. Representative Ag $3d_{5/2}$ EDC's for 0.5 Å Ag on Xe as a function of Xe layer thickness. The inset summarizes the energies of peaks *A* and *B*. The solid line in the inset reflects the calculated change in energy due to an image charge. The energy scale was shifted 0.5 eV to compare with the data.

Insight into the distribution of Ag clusters in and on the Xe layer can be gained by measuring the Ag emission as a function of time for different temperatures. For those studies, the Xe layers were formed, the sample temperature was set at a value between 25 and 50 K, and Ag clusters were grown and their emission was measured at that temperature. Figure 3 summarizes the results for 0.5 Å Ag on 50 Å Xe for measurement at 50 K. The deposition of 0.5 Å Ag on 50 Å Xe reduced the substrate intensity by ~10%. Desorption of Xe or Ag was not observed, as GaAs emission was unchanged at later times. The upper EDC was obtained immediately after growth and is equivalent to that of Fig. 1. With time, however, the EDC's showed remarkable line-shape changes as feature *A* diminished relative to feature *B*. Line-shape analysis showed almost no variation in the energy of peak *A*, with small changes of peak *B* that might indicate slow aggregation in the Xe. Feature *A* decreased until ~6 h after deposition, then attained the line shape shown at 12 h in Fig. 3. The inset of Fig. 3 summarizes changes in the intensity of peak A for different amounts of Ag and annealing temperatures. The same behavior shown by the EDC's was observed for 0.25 Å Ag deposited onto 30 Å Xe at 50 K, but saturation was reached by 4 h for the thinner Xe layer. However, for clusters formed and measured at 25 K, the rate of decrease was slower than at 50 K, and saturation was not reached during the 8-h experiments. This rate was essentially the same for deposition of 0.25 and 0.4 Å Ag on Xe (at 25 K). The fact that the behavior was independent of deposition indicates that the clusters are isolated from each other at these coverages (~80 Å separation between clusters).

The results of Fig. 3 demonstrate that metallic clusters formed on the Xe layer are attracted to the substrate. (Sintering and changes in cluster shape are also possible, but such effects could not produce the observed reduction in Ag emission.) Additional evidence for the sinking of the clusters in the Xe layer can be found by examining the Xe emission as a function of time and annealing temperature. Prior to Ag deposition, the energy of the Xe $3d_{5/2}$ core level (for Xe on GaAs) was 671.4 eV below E_F (675.5 eV from the vacuum level) and its FWHM was 1.1 eV. After Ag deposition, there was an increase in the Xe $3d_{5/2}$ linewidth and there was an overall shift to higher binding energy. The substrate As $3d$ binding energy remained the same, showing that macroscopic charging was not occurring. Deconvolution of the Xe $3d_{5/2}$ line shape required a new component at ~0.5 eV higher binding energy due to the interaction of Xe with the clusters,[19] with the unshifted Xe component initially comprising only ~20% of the total emission. As the intensity of peak A decreased, the Xe $3d$ centroid shifted back to lower binding energy and the intensity of the shifted Xe component decreased. Indeed, the shifted Xe $3d_{5/2}$ component decreased at the same rate as the intensity of peak A for 0.25 Å Ag on 50 Å Xe/GaAs at 25 K. This indicates that the shifted Xe component originates from atoms in the vicinity of the Ag clusters. The large change in Xe line shape for small amounts of deposited Ag suggests that the effect of Ag extends beyond the layer of Xe contacting the clusters. Finally, we note that these results for Ag/Xe are consistent with those for other metals where it was postulated that Xe atoms coat the surface of clusters grown on Xe. Energetically, this is favored since Ag—Xe bond energies are twice those of Xe—Xe bonds.[6]

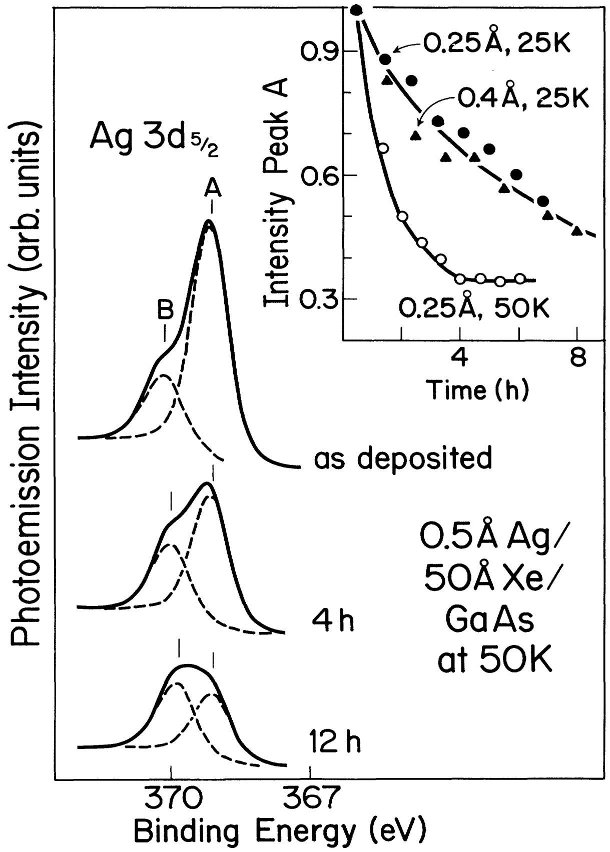

FIG. 3. Ag $3d_{5/2}$ EDC's for 0.5 Å Ag on 50 Å Xe showing the decrease in peak A with time for measurements at $T = 10$ K. The inset shows the rate of decrease of peak A as Ag clusters are drawn toward the GaAs substrate. Measurements for different coverages show that the rate of sinking into the Xe is not altered by the amount of Ag. Results for different temperatures reflect greater emission when the Xe is more pliable.

The results of Fig. 3 make it possible to approximate the final position of the clusters after they have reached the steady-state condition. Although these are very crude estimates since such cluster movement can result in different cluster configurations and shapes,[20] they indicate that the clusters are drawn into contact with the buried GaAs surface. For example, for 0.5 Å Ag on a 50-Å Xe layer at 50 K, peak A was reduced to 30% of its initial intensity after 6 h, as shown in Fig. 3. This is consistent with what would be expected if the ~18-Å-diameter clusters reached the GaAs surface and were covered by a ~32-Å Xe layer. Corresponding estimates for clusters grown at 50 K on a 30-Å Xe layer show an equivalent final-state configuration with Ag clusters in contact with the substrate and covered by Xe.

Figure 4 depicts the formation of a Xe layer on GaAs and the growth of Ag clusters on that layer. Initial depo-

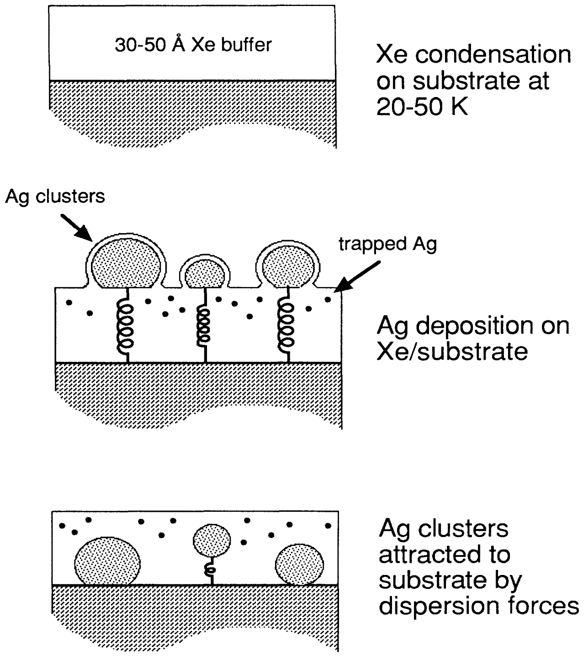

FIG. 4. Schematic diagram showing Xe condensation on GaAs. Ag deposition onto the Xe buffer layer produces Ag clusters on the surface and isolated atoms that are trapped within the matrix. A layer of Xe coats the clusters to reduce the surface free energy. With time, the clusters are drawn through the Xe matrix until they contact the substrate. The springs represent the van der Waals force of attraction.

sition yields Ag clusters that are covered with a Xe skin, as well as embedded Ag atoms. These clusters then sink into the Xe layer with time. The final configuration of clusters in contact with the substrate results in a thinner Xe layer over the clusters. Such motion requires that the Xe layer is pliable enough that a cluster can travel through it when there is a net force between the cluster and the substrate. That force, schematically represented by the springs in Fig. 4, is the van der Waals force.[21,22] As discussed in the context of surface forces and the attraction of macroscopic objects in close proximity, the van der Waals attraction is separable into a material-dependent factor, expressed by the Hamaker constants, and a geometric factor. For the attraction between a sphere of radius R and a plane, the force varies as x^{-2} for distances that are small compared to R. For larger values of x, the force varies as x^{-4}. Although the Hamaker constants have been calculated for many materials, the effects of a three component system such as Ag clusters on Xe on GaAs are not easily derived.[21] However, the van der Waals attraction between a neutral metal cluster of radius 10 Å situated 30 Å away from a GaAs substrate is the same magnitude as the electrostatic attraction between a charged cluster and its image.

The temperature dependence of the cluster motion arises from the pliability of the Xe layer. The compressibility of solid Xe is ~100 times greater than is typical for metals, indicating that the Xe film can undergo substantial deformation under load.[10] Typically, plastic deformations do not occur for temperatures less than $\sim\frac{1}{2}$ the melting point T. Here, the temperatures are ~0.15–0.3 of the bulk melting temperature and the samples are in the form of thin films. It is plausible that plastic flow is likely, particularly at 50 K, consistent with the experimental observations. Since the attraction is proportional to volume and the deformation resistance depends on area, the larger clusters will be drawn to the substrate more rapidly. This can account for the attenuation of peak A and the relative invariance of peak B. Such behavior is analogous to the sinking of colloidal particles in viscous media.

In summary, these results have shown that Ag deposition on Xe produces metallic clusters in the surface and atoms or small clusters that are embedded in the layer. The clusters are drawn through the Xe to the surface by van der Waals forces, particularly at higher temperatures when the Xe is more plastic. Smaller clusters and atoms in the Xe are less affected. These studies illustrate the unique ability of photoemission to detect such changes in the distribution of clusters on their supporting layer.

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