Rapid deterioration of metallic surfaces induced by intense ultraviolet radiation

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We report rapid deterioration of metallic surfaces on irradiation with ultraviolet light. Very fast degradation of the Shockley state of Cu(111) is observed during photoemission at low temperature. A different evolution of the Shockley states during annealing and cooling was also discovered. These observations seem to favor a mechanism based on photon-stimulated chemisorption of hydrogen on the surface. We suggest that this mechanism affects all experiments involving intense radiation and might become a major obstruction for future experiments with microfocused beams.

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Angle-resolved photoelectron spectroscopy (ARPES) (Ref. 1) is a powerful tool to probe system properties that are closely related to electronic structure such as superconductivity, electron-phonon coupling, work function, surface reactivity, etc. Along with many other techniques, ARPES benefits from constant advances in the technology of synchrotron radiation. The beamlines and insertion devices of third-generation storage rings generate intense monochromatic radiation that greatly decreases the duration needed to collect data and allows tests of dynamic modifications of the system properties of small samples. Nevertheless, the possible alteration of samples resulting from prolonged exposure to radiation is always a concern. An extensive literature has been published on radiation-induced modification of, and damage to, sensitive samples such as macromolecular crystals[2] and photoresists.[3] Although metallic samples are considered to resist radiation damage, earlier studies have shown that metallic surfaces exhibit deterioration under irradiation with ultraviolet photons at low temperature but with contradictory conclusions.[4,5] Surface deterioration is typically accompanied with broadening or disappearance of surface-related signals. Overlooking the influence of surface deterioration during measurements can produce improper or even erroneous interpretation of experimental data.

In this paper, we report a mechanism for *rapid* deterioration of metallic surfaces during photoemission. Depending on the surface temperature, the rate of deterioration that this mechanism causes can be much greater than that caused by adsorption of contaminants, which is a common mechanism for surface deterioration in an ultra-high-vacuum (UHV) environment. The surface of interest is Cu(111), but a Cu(111) surface partially covered with Ag was chosen for testing. The surface of Ag-covered Cu(111) served as an internal reference, and this advantage of the choice became obvious while analyzing the deterioration of the Cu(111) surface. The surface of Ag/Cu(111) is characterized with its Shockley states. The Shockley-type surface states are electronic states that appear in the projected energy gap of the bulk band around the $\bar{\Gamma}$ point on the (111) surface of noble metals due to the termination of the crystal by the surface.[6] The binding energy and linewidth of the Shockley states are very sensitive to surface order and composition;[5,7–9] the evolution of the surface can be characterized by monitoring the change in its Shockley states. We observed a rapid degradation of the Shockley state of Cu(111) during photoemission at temperatures less than 220 K. A different evolution of the Shockley states during annealing and cooling was also discovered. All these observations favor a mechanism based on photon-stimulated chemisorption of hydrogen on the surface. We suggest that this mechanism of surface deterioration affects all investigations of a surface involving intense radiation.

Our experiments were performed in an UHV end station installed on Beamline 21B1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Radiation generated from an undulator was focused to a beam of size $100\times200\ \mu\text{m}^2$ at the sample position. All measurements were performed with photons of energy 21 eV, of which the flux is more than 1×10^{12} photons s^{-1}.[10] The storage ring of NSRRC was operated in the "top-up" mode, in which the current in the storage ring is maintained constant; the beam flux and position are presumed constant. The base pressure of the system was better than 6×10^{-11} torr. The pressure was $\sim1\times10^{-10}$ torr during photoemission measurements, due to a slight additional gas load from the beamline. The reading of a residual gas analyzer indicated that H_2 dominated the residual gas, and signals of CO/N_2 and CO_2 were visible; the intensity of H_2 was more than ten times that of other species. Photoemission spectra were recorded with an electron-energy analyzer (Scienta SES200) equipped with a two-dimensional channel plate and a charge-coupled-device camera; the angular resolution was 0.125°. The settings of the analyzer and the beamline were kept the same throughout our experiments to make the intensities of all spectra directly comparable, with possible small uncertainty caused by reproducibility of the sample position and orientation at varied temperatures. A Cu(111) single crystal of diameter 1 cm was cleaned with cycles of Ar ion sputtering and annealing. Silver was evaporated from a Knudsen crucible; its rate of deposition was calibrated with the evolution of the Shockley states on Ag/Cu(111).[8,11] The sample was prepared on depositing 0.5 monolayer (ML) of Ag on Cu(111) and subsequently annealing to 450 K. After annealing, clean Cu(111) and Cu(111) covered by Ag at 1 ML, denoted "1-ML Ag/Cu(111)," coexist on the sample surface.[8] The surface, characterized with the Shockley states of Cu(111) and 1-ML Ag/Cu(111), might deteriorate after prolonged measurements. The ordering of the surface was restored on briefly annealing

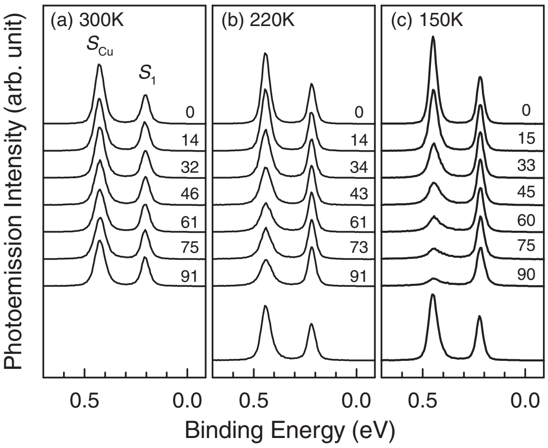

FIG. 1. Stacked plots of spectra of normal emission measured on 0.5-ML Ag/Cu(111) at (a) 300 K, (b) 220 K, and (c) 150 K. The number beside each curve indicates the duration (in minutes) of exposure of the sample to radiation before the measurement of the spectrum. The bottom spectra in (b) and (c) were measured at a new location on the sample after completion of the measurements of the second spectra from the bottom. The two peaks in each spectrum are the Shockley states of Cu(111) and 1-ML Ag/Cu(111), labeled S_{Cu} and S_1, respectively.

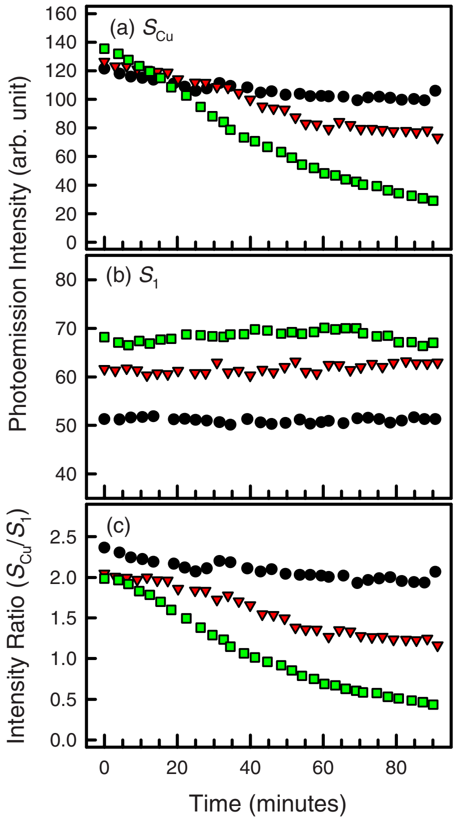

FIG. 2. (Color online) (a) and (b) show the integrated intensities of S_{Cu} and S_1, respectively, as functions of time under irradiation. (c) shows the intensity ratio between S_{Cu} and S_1 as functions of time under irradiation. The measurements were performed at temperatures 300 K (black circles), 220 K (red triangles), and 150 K (green squares).

the sample to 450 K. The sample was aligned on measuring the dispersion of its Shockley states; after alignment, the sample was moved to ensure that the measurement of each data set was initiated on a fresh surface.

Figure 1 illustrates how the Shockley states evolve with prolonged exposure to radiation at various temperatures; the same sample [0.5-ML Ag/Cu(111)] was used in all measurements. The sample was refreshed on annealing to 450 K then cooled and maintained at the specified temperature. The sample was then continuously exposed to photons of energy 21 eV for about 90 min; photoemission spectra were collected during that exposure. After exposures at 220 and 150 K, the sample was moved ~1.5 mm vertically; a further spectrum was recorded and is plotted at the bottom of the stacked plot. Each spectrum in Fig. 1 comprises two peaks, labeled S_{Cu} and S_1, pertaining to the Shockley states of Cu(111) and 1-ML Ag/Cu(111), respectively.[8] Dissimilarity in the evolution of spectra with temperature is evident: the spectra remain essentially unchanged at 300 K, whereas S_{Cu} degrades noticeably at 220 and 150 K. Although showing a slight broadening, the bottom spectra in Figs. 1(b) and 1(c) resemble the top spectra measured at the beginning of the experiments, which is a strong indication that rapid degradation of S_{Cu} exists only in the area under irradiation. The degradation was quantified on fitting each feature with a Voigt line shape; the integrated intensities (the area under the curves) of S_{Cu} and S_1 are plotted against the duration of irradiation shown in Figs. 2(a) and 2(b), respectively. The intensity of S_{Cu} varies little at 300 K but decreases substantially at 150 K, agreeing with the observation in Fig. 1. The intensity of S_1 remains roughly the same with small fluctuations, implying that the 1-ML Ag/Cu(111) surface deteriorates little during these measurements. One thing worth mentioning is that S_1 does degrade noticeably during photoemission at a sample temperature less than 90 K (data not shown). When the spectra were collected with the storage ring operating in the top-up mode, as mentioned above, the normalization of data required little effort. However, for measurements performed with a varying photon flux—e.g., when the storage ring operated with a decaying current—the data in Fig. 2(a) required normalization to become meaningful. In this work, S_1 served as an internal reference, and the degradation of S_{Cu} at various temperatures was readily normalized and compared on taking an intensity ratio between S_{Cu} and S_1. The variation in these ratios with temperature, plotted in Fig. 2(c), reinforces the observation that, during photoemission, the Cu(111) surface rapidly deteriorates at 220 and 150 K but to little or no extent at 300 K.

To investigate the nature of the photon-stimulated deterioration of this surface and to demonstrate how this deterioration causes problems of measurement, we performed the following test. We implemented a standard routine in determining the electron-phonon coupling strengths in Cu(111) and in 1-ML Ag/Cu(111) on measuring the dependence on temperature of the linewidth of their Shockley states.[12] Figure 3 is a stacked plot of photoemission spectra measured at various temperatures. The measurement was completed with an annealing and a cooling cycle. As observed in the figure, both Shockley states move toward the Fermi level (zero binding energy) at higher temperatures,

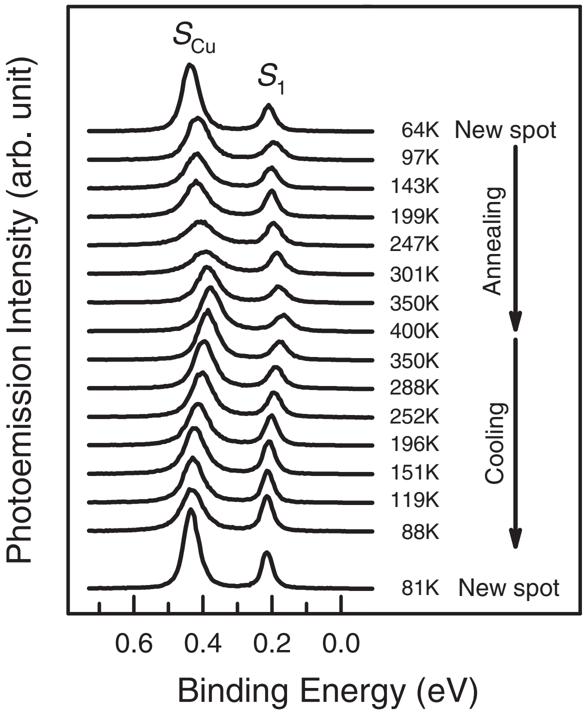

FIG. 3. A stacked plot of spectra of normal emission measured on 0.5-ML Ag/Cu(111) during annealing and cooling. The sample temperature is labeled at the right of each spectrum. The "New spot" indicates that the spectrum was measured at a new location on the sample. The Shockley states of Cu(111) and 1-ML Ag/Cu(111) are marked S_{Cu} and S_1, respectively.

agreeing with previous work.[13] The widths of both states increase with increasing temperature, as expected because of the reduced lifetime of Shockley states at higher temperature.[12] The width of S_{Cu} is, however, noticeably wider during annealing. Moreover, after the sample was moved ~1.5 mm vertically, indicated as "New spot" in Fig. 3, at the end of the cooling cycle, the width of S_{Cu} decreased significantly, but S_1 remained unchanged. In addition, the associated spectrum resembles the top spectrum in the stacked plot. This is further convincing evidence that only the Cu(111) surface deteriorates rapidly under photon irradiation.

The dependence of the linewidths of the Shockley states on temperature is determined from fitting the spectra in Fig. 3. Each spectrum was fitted to two Voigt line shapes with the Gaussian width (full width at half maximum) fixed to the instrumental resolution (~30 meV); the fitted Lorentzian widths (full width at half maximum) were assigned to the linewidths of the Shockley states. The results from the fitting, plotted in Fig. 4, show noticeably the difference in the temperature-dependent variation in the linewidths between S_{Cu} and S_1. Furthermore, the widths of both S_{Cu} and S_1 vary differently between annealing and cooling. For example, the width of S_{Cu} is ~90 meV at 280 K during annealing but only ~50 meV at a similar temperature during cooling. The main contributions to the linewidth are electron-electron interaction, electron-phonon interaction, and impurity or defect scattering.[12] At the limit of high temperature, the width (ΔE) depends linearly on the temperature (T); the electron-phonon coupling parameter λ is determined by $d\Delta E/dT = 2\pi k_B \lambda$, in which k_B is Boltzmann's constant.[12] Agreeing with the prediction, the width of S_1 depends linearly on the temperature when the annealing temperature is above 200 K and when the cooling temperature is above 120 K. From the slope determined through linear regression, the result shown as a dashed blue line in Fig. 4 yields $\lambda = 0.14$, which is near the reported values for bulk Cu (0.15), bulk Ag (0.13),[14] the Cu(111) Shockley state (0.14~0.16),[12,15] the Ag(111) Shockley state (0.12),[15] and thick Ag films on Cu(111) (0.17~0.23),[16] but the behavior of the width of S_{Cu} deviates strongly from the prediction. During annealing, this width increases disproportionately until near 300 K and then decreases rapidly. This large fluctuation in the linewidth makes problematic the evaluation of λ with photoemission at low temperature for S_{Cu}. A similar variation in the width of S_1 during annealing is observed, but at a temperature less than 180 K.

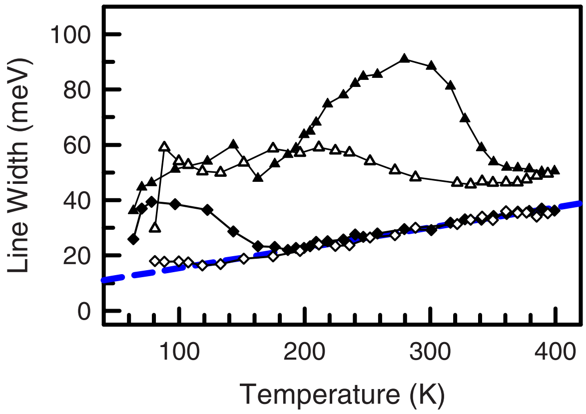

FIG. 4. (Color online) Linewidths of Shockley states as functions of sample temperature. The linewidths of the Shockley states of Cu(111) (S_{Cu}) and 1-ML Ag/Cu(111) (S_1) are shown as triangles and diamonds, respectively. The linewidths measured during annealing and cooling are labeled with filled and open symbols, respectively. The last data point in the cooling cycle was measured at a new spot. The dashed blue line indicates the result from linear regression on the linewidth of S_1 (see text for details).

Few reports have appeared about the mechanism of deterioration of metallic surfaces during photoemission. Two possible mechanisms of deterioration have been reported, of which one is simple structural disorder under ultraviolet irradiation. When Purdie *et al.*[4] monitored the $\bar{M}$ Tamm state of Cu(100) exposed to radiation from a helium discharge lamp, they observed a deterioration of the surface at 10 K but not at 70 K and above; they suggested that the structural disorder was induced by the radiation: the concentration of structural defects decreased and the surface became thermally healed through annealing at elevated temperatures. The other mechanism of deterioration is adsorption of contaminants. Nicolay *et al.*[5] reported a modification of the Shockley state on the (111) surface of noble metals at 30 K while a helium discharge lamp was operating; they inferred that the surface deterioration was caused by adsorption of activated molecules of residual gas, such as hydrogen, generated from the helium discharge lamp. Furthermore, they excluded ultraviolet radiation as the major cause of the surface aging and suggested that this deterioration might be avoided on utilizing synchrotron radiation as a light source. Both mechanisms of surface deterioration mentioned above fail to explain our results satisfactorily. The data in Figs. 1 and 2 indicate that the Cu(111) surface deteriorates noticeably under ultraviolet irradiation at a temperature as high as 150 K, and Figs. 3 and 4 show that the surface disorder of Cu(111) is greatly enhanced, not suppressed, when the surface is annealed at elevated temperatures. These observations do not support the thermal healing of simple structural disorder but favor the adsorption of contaminants as the major cause of surface deterioration. Furthermore, our experiments incontestably demonstrate that the rapid deterioration of Cu(111) is associated with intense synchrotron radiation, and in our system there is no obvious source of activated gas molecules, such as a He lamp used by Nicolay *et al.*[5]

Because only the Shockley states were explored in our experiments, it is difficult to determine indisputably which contaminants are involved in the photon-stimulated surface deterioration, but the experimental results provide clues to some possible suspects. First, in our well-maintained UHV system, the residual gas contains few active gas molecules, and the surface of a noble-metal stays clean for tens of hours; as a result, during the photon-stimulated deterioration of the surface, the contaminants come mainly from the activated residual gas dominated by hydrogen. Secondly, during the annealing tests performed in Figs. 3 and 4, the widths of the Shockley states underwent a large increase and then decreased to the values for a clean ordered surface; this test can be considered to constitute temperature-programmed desorption. The result indicates that the desorption of the contaminants from Cu(111) and Ag/Cu(111) is complete at ~350 K and ~180 K, respectively; these numbers match satisfactorily the temperatures for chemisorbed hydrogen atoms to desorb from Cu(111) [280~350 K (Refs. 7 and 17)] and Ag(111) [180 K (Ref. 18)]. According to the above arguments, it is reasonable to consider chemisorbed hydrogen atoms to be a principal contaminant involved in the rapid deterioration of metallic surfaces observed in our experiments.

A summary of the above discussion provides a scenario for the observations in our measurements. Molecular hydrogen is the dominant species in the residual gas of a well-maintained UHV system. For Cu(111) and Ag(111), a large activation barrier prevents chemisorption of hydrogen,[7,18,19] but physisorption of hydrogen molecules might occur with a small sticking coefficient until the surface attains a low temperature. During photoemission, hydrogen molecules are energized to overcome the activation barrier and become chemisorbed on the surface. The chemisorbed hydrogen atom remains on the surface until it warms to the desorption temperature. Before the chemisorbed hydrogen is completely desorbed, the mobility of hydrogen on the surface increases with increasing temperature, severely broadening the surface-related signals, e.g., the Shockley states, through a strong impurity or defect scattering. In addition, the amount of hydrogen sticking on the surface and involved in the surface deterioration depends on the history of the surface—e.g., how long the surface has been held at a particular temperature—and it predicts directly the varied behavior of the linewidth during the annealing and cooling cycles.

Issues remain unanswered. Our experiment demonstrates unambiguously that the rapid deterioration of metallic surfaces is associated with an exposure to photons, and the temperature dependence of the measurements indicates that the likely culprit for this deterioration is hydrogen chemisorbed on the surface. Nevertheless, our work does not exclude a possibility that other chemical species common in an UHV system might also participate in the deterioration. In addition, although our measurements seem to favor chemical adsorption as the major cause of the surface deterioration, they cannot completely exclude the structural disorder induced by photons at low temperature; both mechanisms of deterioration might occur concurrently but have varied extents of influence. The role of the photon in the mechanism of deterioration is also unknown. How do photons help hydrogen molecules overcome the activation barrier to become chemisorbed? Does a photon energize hydrogen molecules directly or through exciting photoelectrons? ARPES employed in our experiments apparently lacks the capability to clarify these issues.

The advantages of using Cu(111) partially covered with Ag, instead of clean Cu(111), for testing are evident during characterization of the deterioration of the surface. The two Shockley states on Ag/Cu(111), S_{Cu} and S_1, in a single spectrum are explored under the same experimental conditions. In this study, S_1 is less susceptible and serves as an internal reference for intensity and linewidth. Only with this reliable reference can we investigate with confidence the degradation of S_{Cu} shown in Figs. 2 and 4. In addition, with the chemisorbed hydrogen as the possible suspect responsible for the surface deterioration, the measurement performed in Figs. 3 and 4 is considered to constitute temperature-programmed desorption; the desorption of chemisorbed hydrogen on Cu(111) and 1-ML Ag/Cu(111) becomes explored concurrently.

All photoemission measurements on surfaces are subject to the mechanism of surface deterioration that we here report. The extent of the effect of this mechanism on experiments depends on several factors: the interaction between hydrogen and the surface, the surface temperature, the photon flux density, etc. The surface deterioration associated with the proposed mechanism is typically overlooked or unobserved, likely, because of the small photon flux density and the small sticking coefficient of hydrogen under common conditions. When a low temperature is employed for the ultimate energy resolution and when intense radiation becomes available from a third-generation storage ring or a free-electron laser, only a brief interval is required to accumulate sufficient contaminants or structural defects on a surface to make the deterioration observable, even before completing the first photoemission measurement. The photon flux density will increase greatly with the construction of microfocusing beamlines that focus radiation to a diameter less than 10 μm. The surface deterioration, according to the proposed mechanism, is likely to become a major obstacle to the success of future experiments on surfaces utilizing microfocused beams.

In summary, we report the observation of metallic surfaces rapidly deteriorating under irradiation of ultraviolet photons at low temperatures. We investigated systematically the rapid degradation of the Shockley states on 0.5-ML Ag/Cu(111). A scenario based on chemisorption of hydrogen on surfaces stimulated by photons explains the experimental observations. We suggest that the mechanism of deterioration is universal, but its influence varies with several factors.

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