Rapid Deterioration of Metallic Surfaces Induced by Intense Ultraviolet Radiation

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We report a mechanism for *rapid* deterioration of metallic surfaces during photoemission. The surface of interest is Cu(111), but a Cu(111) surface partially covered with Ag was chosen for testing. The surface of Ag/Cu(111) is characterized with its Shockley states, of which the binding energy and line width are very sensitive to surface order and composition; the evolution of the surface can be characterized by monitoring the change of 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 on Beamline 21B1. All measurements were performed with photons of energy 21 eV; the beam flux and position are presumed constant. The base pressure of the system was better than 6×10^{-11} torr. 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.

Figure 1 illustrates how the Shockley states evolve with prolonged exposure to radiation at various temperatures. After exposures at 220 K 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. 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.

Figure 2 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, the width of S_{Cu} is noticeably wider during annealing. The dependence of the line widths of the Shockley states on temperature is determined from fitting the spectra in Fig. 2. The results from the fitting are plotted in Fig. 3. The line widths 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 line widths measured during annealing and cooling are labeled with filled and open symbols, respectively. The results show noticeably the difference in the temperature-dependent variation of the line widths between S_{Cu} and S_1. Furthermore, the widths of both S_{Cu} and S_1 vary differently between annealing and cooling.

The widths of the Shockley states underwent a large increase and then decreased to the values for a clean ordered surface; our measurement can be considered to constitute temperature-programmed desorption (TPD). 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) and Ag(111). The results suggest that chemisorbed hydrogen atoms are likely a principal contaminant involved in the rapid deterioration of metallic surfaces observed in our experiments.

We believe that all photoemission measurements on surfaces are subject to the mechanism of surface deterioration that we here report. The surface deterioration according to the proposed mechanism is likely to become a major obstacle to the success of future experiments on surfaces utilizing micro-focused beams.

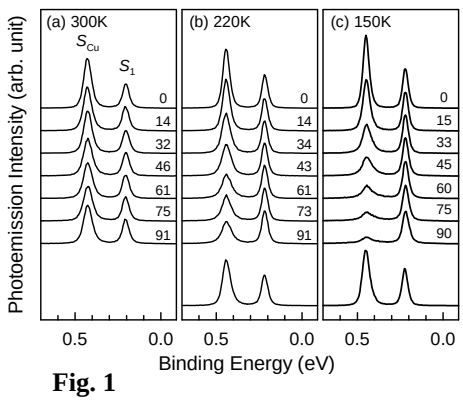

Fig. 1

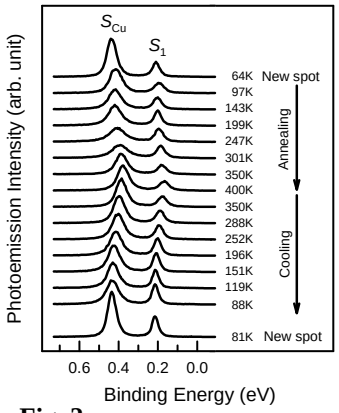

Fig. 2

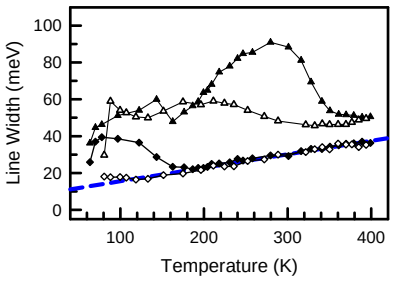

Fig. 3