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PEEM study of work function changes in Cu, Au and Pd metal surfaces with surface acoustic wave propagation

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Abstract

The effects of surface acoustic wave (SAW) on the work function of Cu, Au and Pd metal surfaces with different surface structures were studied by photoelectron emission microscopy (PEEM). SAW propagation produced bright PEEM images for Cu, Au and Pd metal surfaces consisting of high-index planes and step sites, whereas it yielded dark images for the metals exposing low-index planes, indicating that the SAW enhanced photoemission from rough metal surfaces containing coordinatively-unsaturated metal atoms and lowered that from densely packed smooth metal surfaces. Changes in the PEEM images with SAW-on and SAW-off were reversible and were associated with decreases and increases in the work function of the metal surfaces, respectively. The SAW caused periodic and vertical lattice displacement, and it was demonstrated that large lattice displacement was responsible for work function changes from coincidence between the patterns of photoemission and lattice displacement. A mechanism for work function changes is proposed on the basis of effects on the spatial structures and electronic properties of metal surfaces.

Keywords: Surface acoustic waves; Piezoelectric effect; Photoelectron emission microscopy; Work function; Surface structures; Copper; Silver; Gold; Polycrystalline surfaces; Metallic films

1. Introduction

Work function is one of the most important surface properties and determines the chemical and physical properties of metal surfaces. It is intrinsic to the metal–metal atom distance and metal atom arrangements. Hence, it is interesting to investigate how the work function of metal surfaces varies as the metal lattice is dynamically distorted.

A surface acoustic wave (SAW) is generated on a poled ferroelectric crystal by imposing rf electric power to interdigital transducer (IDT) electrodes deposited on the crystal, and can cause the lattice distortion of thin metal films deposited on its propagation path. We have previously demonstrated that the SAW is capable of activating thin polycrystalline metal (Ag, Pd, Ni) film surfaces, markedly enhancing their catalytic activities for ethanol and CO oxidation [1–4]. King et al. observed that the SAW enhanced the catalytic activity of a Pt{1 1 0} single-crystal film for CO oxidation [5–8]. Furthermore, it exhibited interesting effects that were able to accelerate a single path in two parallel reaction paths on catalysts. For example, in Cu metal-catalyzed ethanol decomposition, the SAW dominantly enhanced ethylene production with little change in acetaldehyde production [9]. These results strongly suggest that the SAW affects the electronic structures of metal surfaces, and it is thought that the effects on catalyst activation and reaction selectivity are closely associated with changes in the work function. To confirm this, it is useful to determine photoemission characteristics directly related to the work function of metals during SAW propagation.

Photoelectron emission microscopy (PEEM) provides a magnified image of the surface thanks to contrasts in the intensity of photoelectrons emitted from surfaces irradiated by UV light and yields a two-dimensional pattern of

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differences in the work function of metal surfaces [10]. In a previous preliminary study, changes in the intensity of photoemission for a polycrystalline Cu thin film with SAW propagation were observed. The study showed the importance of conducting research to find out whether or not similar SAW effects were observed in other metal systems. Furthermore, the advantages of PEEM can be exploited to seek a positional correlation between lattice distortion and work function changes.

In the present study, a PEEM apparatus was designed to measure the PEEM images of metal surfaces during SAW propagation. Polycrystalline Cu, Au and Pd thin films were deposited on the propagation path of Rayleigh SAW. To investigate the SAW effects on the photoemission behavior of metal surfaces with different surface structures, the metal surfaces were treated in different manners: a smooth surface was produced by annealing, and a rough surface was fabricated by sputtering. To characterize the surface structures of these metal surfaces on an atomic scale, an infrared reflection absorption spectroscopy (IRAS) method was employed using CO as a probe molecule.

2. Experimental section

For the generation of a Rayleigh SAW, a 128°-rotated y-cut $LiNbO_3$ single crystal with a thickness of 0.5 mm was used. The two IDT electrodes, designed to generate an acoustic wave with a wavelength of 200 μm and a frequency of 20 MHz, were fabricated photolithographically on the crystal plane. Polycrystalline Cu, Au and Pd films (13×13 mm) were deposited at a thickness of 80 nm in the middle of the substrate crystal surface between the two IDT electrodes so that the SAW propagated through the metal phase. The metal films were prepared by evaporation of the metals with electron beam heating in vacuum and deposition at a rate of 0.5 nm s^{-1} at 473 K. After deposition, a sample was quickly transferred to the chamber of a separate PEEM apparatus. The metal films were either annealed at 573 K for 2.5 h under ultra high vacuum (UHV) conditions ($<10^{-7}$ Pa) (the metal surface is referred to as an annealed surface) or sputtered at 373 K at 1000 V and then subjected to heat treatment at 573 K for 2.5 h in UHV conditions (the surface is referred to as a sputtered surface). Experiments were carried out using annealed and sputtered samples prepared separately and were repeated with fresh samples.

A PEEM apparatus was designed to measure the photoemission characteristics during SAW propagation. Fig. 1 schematizes the PEEM system, together with a sample holder. A SAW sample was mounted on a copper plate furnished with a PBN heating plate. The temperature of the sample was changed from room temperature to 573 K. The SAW sample was placed just below the PEEM optics system to be as close as possible (4 mm) to the inlet, and irradiated at an incident angle of 70° using a 200 W deuterium lamp. The ejected electrons introduced into the PEEM lens system were captured by a phosphor screen.

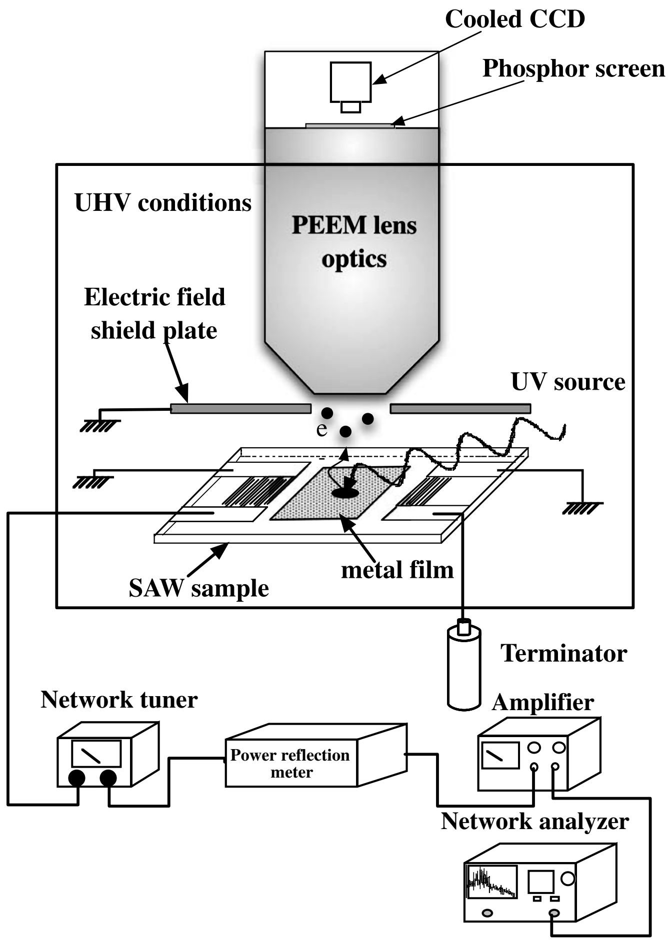

Fig. 1. The schema of a PEEM apparatus and an electric circuit for SAW generation.

The brightness changes in PEEM images caused by photoelectrons were monitored with a cooled CCD camera (Hamamatsu Orca-ER). Measurements were performed at room temperature under UHV conditions ($<1 \times 10^{-8}$ Pa). The SAW was generated at a rf power of 0.2–1.0 W. The PEEM images and intensity changes with SAW-on and SAW-off were taken repeatedly to confirm reproducibility.

3. Results and discussion

In a previous study [11,12], we used infrared absorption spectroscopy (IRAS) for CO adsorption in order to determine the atomic-scale structure of polycrystalline metal surfaces prepared by annealing and sputtering since the vibration frequencies of the adsorbed CO used as a probe molecule provide information on the structure of Cu surfaces. Only a symmetric single peak was observed at 2070 cm^{-1} on an annealed Cu surface, whereas a complex spectrum consisting of four peaks at 2072, 2087, 2097, and 2104 cm^{-1} was obtained for a sputtered Cu surface. On the basis of the comparison of CO adsorption on Cu single crystals, the single peak at 2070 cm^{-1} for the