Effect of Vapor Adsorption on the Photoelectron Emission from Gold in Ambient Atmosphere

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Photoelectron emission from Au was measured in ambient atmosphere under irradiation of ultraviolet light from a Hg lamp. The emission was greatly influenced by the adsorption of organic and inorganic vapors. The adsorption of cyclohexene showed a significant, but gradual increase of photoelectron emission. On the other hand, the adsorption of acetone reduced photoelectron emission irreversibly to near zero. The change of the photoelectron emission could be interpreted in terms of the change of the work function.

Photoelectron emission in vacuum have been known for a long time and have many applications. Recently, photoelectron emission in ambient atmosphere have been attracted much attention as a principle of a new method to produce ultra clean spaces for handling silicon wafers.[1] Fine dusts and particles are charged by photoelectrons and are collected by an opposite electrode which is biased to positive. This method works without any mechanical device such as fans and filters. Although Au films are promising materials for the photoelectron emitter, their lifetimes are not sufficiently long: photoelectron current gradually decreased probably due to organic contamination adsorbed on the surface.[1]

Effects of adsorbed molecules on photoelectron emission and work functions in ultra high vacuum (UHV) have been extensively studied.[2-6] Adsorption of polar molecules frequently decreases work function of clean metal surface in UHV. For example, submonolayer of pyridine adsorbed on Au induced 0.7 eV of decrease of the work function.[3] CH_3I dissociatively adsorbed on Au (100) and reduced the work function by ca. 1.0 eV.[4] H_2O decreased the work functions of Ru(001)[5] and K deposited Pt (111).[6] A few studies have been reported about photoelectron emission in ambient atmosphere. Fundamental behaviors of Au thin films were studied using a specially designed detector.[7,8] Photoelectron emission of Si were measured after dipping into organic solvent and drying.[9] In the present study, we measured photoelectron emission as well as work functions for Au thin films in air and have found that the photoelectron current was extensively enhanced or suppressed by adsorbed molecules.

Au thin films on Ti plates were prepared by thermal deposition in vacuum. The thickness was ca. 100 nm. The Au deposited plate (1 x 5 cm^2) and a stainless grid were placed at a distance of 1 cm in a transparent quartz gas flow cell (5 cm in diameter, volume: ca. 500 cm^3) as shown in Figure 1. An Al shield plate was inserted along the inner wall of the quartz cell and was grounded to avoid charging of the inner wall of the cell. The grid was biased to +100 V dc against the Au film and the sample was irradiated with a Hg lamp (254 nm, 4 W) from the outside of the quartz cell. Photoelectron current between the sample and the grid was measured with an electrometer (Keithley 6517 A). The gas flow (200 cm^3 min^{-1}) was switched between dry air (atmospheric pressure) and air containing 0.1 - 3 Torr of organic or water vapor during the photoelectron measurement.

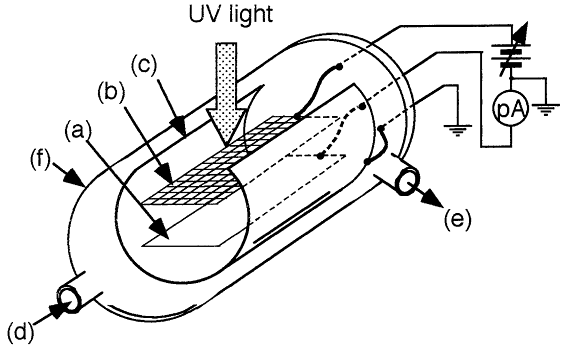

Figure 1. Schematic illustration of a cell for photoelectron current measurements. (a) sample, (b) stainless grid, (c) shield, (d) gas inlet, (e) gas outlet, (f) quartz cell.

Work function in atmospheric pressure was determined as the threshold photon energy for photoelectron emission;[10] the monochromated uv light (180 - 400 nm) from a 500 W Xe lamp coupled with a grating was used for this measurements. It was confirmed that no current was detected without uv light irradiation, i.e. there was no leak of current.

Figure 2 shows the effect of various molecules on the photoelectron current. As shown in Figure 2a, the introduction of 0.5 Torr of ethanol increased the current from 510 to 610 pA rapidly. This change was reversible: the current rapidly decreased when the gas was switched to dry air without ethanol. H_2O gave a very similar result.

It should be noted that cyclohexene induced a significant increase of the photoelectron current. As shown in Figure 2b, ca. 41% of enhancement was observed when 0.5 Torr of cyclohexene was introduced with dry air. The change is much slower than that for ethanol (note the difference in the time scale of Figures 2a and 2b).

Acetone showed an effect totally different from the above two cases. An introduction of 0.5 Torr of acetone resulted in a drastic reduction of photoelectron current to almost zero (Figure 2c). The change is much slower than that for ethanol and H_2O. The current did not recovered completely and reached only 10% of the initial value even after removal of acetone from the gas phase. It was confirmed that alkane such as *n*-hexane and cyclohexane have no effect on the photoelectron current.

Work functions were measured in the presence and absence of 0.5 Torr of organic vapors in dry air. Before the introduction of the organic vapors, the work function of the Au thin films was 4.57 eV. As for ethanol, the change of work function ($\Delta\Phi$) was ca. -0.01 eV. $\Delta\Phi$ for 0.5 Torr of cyclohexene was -0.05 eV, which is five times larger than that for ethanol. On the other hand, 0.5 Torr of acetone gave a large $\Delta\Phi$ by 0.25 eV. This is consistent with the drastic decrease of photoelectron

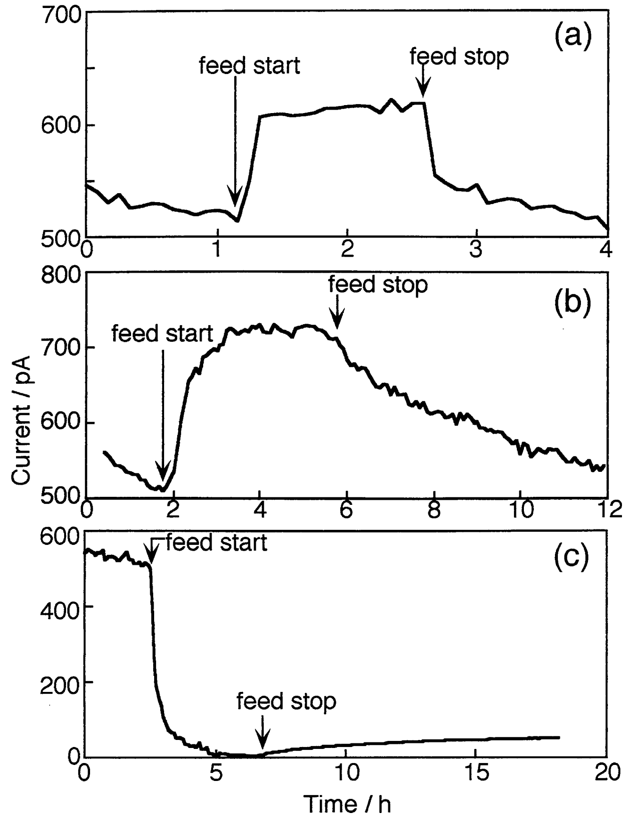

Figure 2. Time course of photoelectron current upon a feed of organic vapors. (a) ethanol, (b) cyclohexene, (c) acetone. Partial pressure, 0.5 Torr. Total flow rate, 200 cm^3 min^{-1}, air balance.

current shown in Figure 2c. The large decrease of the work function was hardly recovered even after removing acetone from the air. This finding is also consistent with the incomplete recovery of the photoelectron current.

As for ethanol and cyclohexene, the effects of their partial pressures on the work function were examined (Figure 3). On the introduction of cyclohexene, the $\Delta\Phi$ changed steeply by -0.12 eV with the increase of the partial pressure to 1.25 Torr, and then changed gradually to -0.14 eV at 2.85 Torr. In accordance with this change, the photoelectron current was drastically increased from 510 to 840 pA, indicating that the significant increase of photoelectron current is due to the large decrease of the work function. The change of work function for the adsorption of ethanol was much smaller than cyclohexene, as shown in Figure 3.

In case of clean surfaces of metals, the dipole moment of adsorbed molecules contributes significantly to the change of work function.[11] In the present findings, cyclohexene influenced work function much more than ethanol and H_2O, although dipole moment of cyclohexene (0.33 D) is much smaller than that of ethanol (1.44 D). The much slower change of photoelectron current for cyclohexene than for ethanol suggests that a slow step such as photochemical reaction on the surface is involved in the mechanism of the unusual enhancement by cyclohexene. The large and irreversible change of the work function of gold by the adsorption of acetone could be ascribed to some irreversible change of the surface induced by the photochemical reaction with acetone.

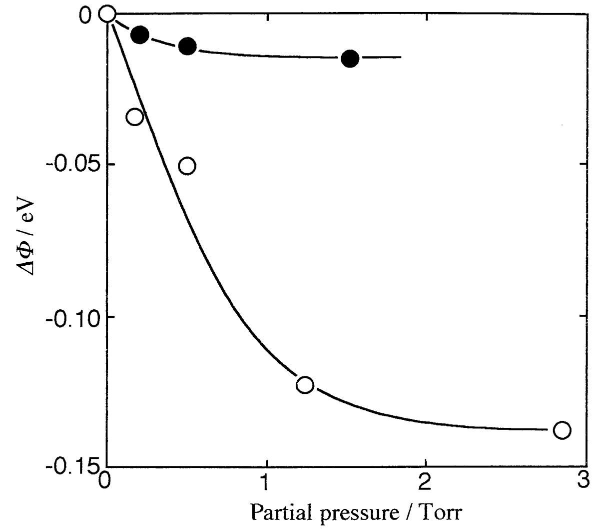

Figure 3. Effect of partial pressure of organic vapors on work function. (○) cyclohexene, (●) ethanol.

The enhancement of the photoelectron emission by the modification of Au surface in air can be a promising phenomenon for the design of a more improved photoelectron emitter in future. Further study on this point is now in progress.

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