Morphological Development and Etching of Gold Thin Film under UV-exposure in Chlorine-based Liquids

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Gold thin film is found to be soluble in chlorine-containing liquid such as 1,2-dichloroethane, NaCl, or HCl solution under illumination, especially UV shorter than 310 nm. We attribute this to the formation of gold chloride and its desorption from the surface. Atomic force microscopy study shows that the grain-like surface morphology evolves during the etch process.

Gold is very important substrate material for the growth of ultrathin films in chemistry. Most self-assembled films are grown on gold surface.[1–4] Also in electrochemical or photochemical deposition, gold films are used as substrates.[5–7] As many applications are in the field of ultrathin films, it is very important to understand the morphology of gold surface when used in various experimental environments. When experiment is performed at an elevated temperature, the grain size of gold thin film can evolve through the annealing process.[7] Or, gold surface can be modified through the chemical reaction when it is submerged in a certain solution.[8] Meanwhile, many experiments have been performed under illumination using gold as substrate.[8–10] Here, light illumination can be provided either for photochemical process or for optical characterization of thin film. However, in these cases, the effect of light on gold substrate has not been considered seriously. This is because substrates are usually stable during film process or characterization. However, we can encounter many cases in which the properties of substrates are modified during thin film deposition or optical characterization. When amorphous silicon films were deposited on zinc oxide substrate using plasma dissociation of silane gas, atomic hydrogen generated from plasma penetrated into zinc oxide to modify the optical properties of substrate through doping, which known as Burstein–Moss effect.[11–13] Also the optical properties of photoresist were modified during the measurement with spectroscopic ellipsometry. In this case, photoresist was developed by the Xe-arc source of ellipsometer itself.[14]

In this letter, thus, we present the effect of light on gold substrate in chemical process. When we used real-time spectroscopic ellipsometry to study the photopolymerization of diacetylene monomer on gold, we noticed that there were small changes in ellipsometry spectrum even before the addition of diacetylene monomer into solvent, 1,2-dichloroethane.[10] There were two light sources in the study, (i) 15-W mercury lamp for photopolymerization, located backside of gold film as shown in Figure 1. (ii) 75-W Xe-arc lamp on spectroscopic ellipsometer. The former has line spectra, one dominates at 253.7 nm. Meanwhile the latter has continuous spectrum covering 250–800 nm range. We found that both light sources have responsibility for the small change in ellipsometry spectra. For further investigation, the same configuration of chemical cell was used as shown in Figure 1 and long-term exposure was performed over a period
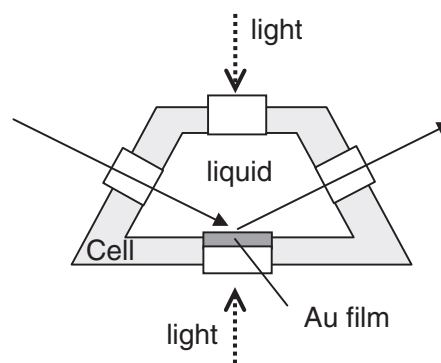

Figure 1. Chemical cell made of Kel-F. The broken arrows indicate illumination from front side (top) and back side (bottom) of gold film. The solid arrows indicate ellipsometry beams entering and exiting through fused silica windows.

of an hour in 1,2-dichloroethane.

For thin gold film (8 nm thick) grown on fused silica glass, the back side of gold film was illuminated by a 15-W mercury lamp, which guaranteed the transmission of light down to 230 nm in wavelength. For thick gold films (100 nm), lamp shined the front side of gold film through the liquid. When 8-nm thick gold film was exposed to the light for ≈90 mins, the film was completely etched away from the fused silica glass as we can see from the evolution of ellipsometry spectrum (Del) measured in real time (Figure 2).
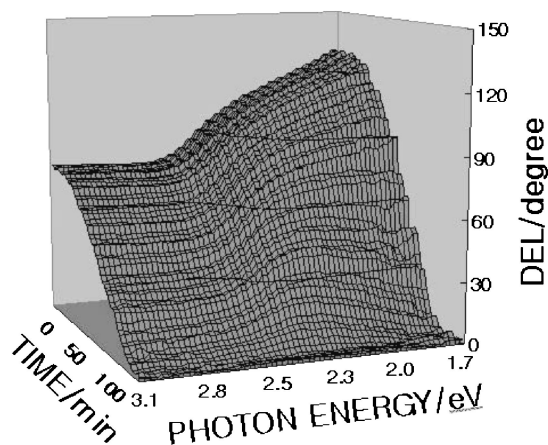
In order to see the wavelength dependency of the etching

Figure 2. Ellipsometry spectrum, Del, over 1.7 to 3.1 eV measured in real time during 100 min exposure to mercury lamp. Almost constant value of Del over photon energy after ≈90 min into exposure shows the optical properties of glass substrate, indicating the complete removal of gold film.

effect, we used cut-off filter ($\lambda_c \approx 310$ nm) to block 253.7-nm line in mercury spectrum. This filter has an I-shaped hole on center to allow 253.7-nm line to pass. We can see from Figure 3 that I-shaped pattern appears as gold film is etched away (left). Therefore, it can be said that mercury lines longer than 253.7 nm are not effective for etching of gold film.
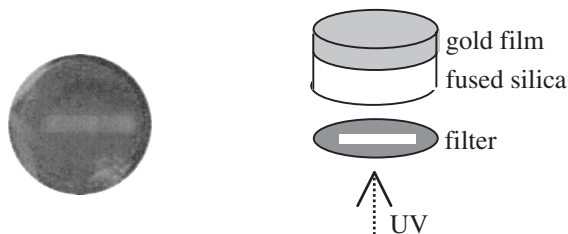
Figure 3. Photograph of 8-nm thick gold film after 30 min into exposure to mercury lamp through filter (left). Dark color shows the area still covered by gold film without being etched. Figure on the right hand side shows the configuration of sample structure and filter with I-shaped hole.

This etching phenomenon was observed in other liquid which contains chlorine such as NaCl or HCl solution, however, not in pure water or alcohol. Also, both thermally evaporated films and sputtered films showed the same etching effect. Compared to the etch rate shown in Figure 2 (≈ 0.9 nm/min), ten times higher etch rate was obtained when an ArF excimer laser was used as light source for 193 nm (60 mJ per pulse). From these experiments, it is plausible that UV light activates the formation of gold chlorides and these desorb from the surface of gold. It is known that mechanical stress develops when the physical or chemical properties of the surface change in liquid environment.[1,15–17] However, more works are needed to understand the nature of gold chlorides and their roles in this etching phenomenon.[18]

In order to see the evolution of surface morphology of gold during UV exposure, we used thick gold film and illuminated light from the front side of film as shown in Figure 1. In this experiment, atomic force microscopy (AFM) measurements were performed ex situ in every 10 mins of exposure to mercury lamp. As we can see in Figure 4, the grain-like surface evolves through the coalescence-like behavior in which grain size grows gradually during exposure. Considering that this phenomenon occurs simultaneously with the etching effect, some of the gold chlorides formed by UV radiation could be reabsorbed onto gold surface and subsequently reduced to gold. We believe this reduced gold is responsible for the coalescence behavior of surface grain morphology. This kind of reaction at gold and gold chloride interface was also observed by Wall et al. from AFM studies, where AFM was used to measure the interfacial electrostatic changes during the absorption of gold chloride on gold and subsequent reduction of gold chloride.[8]

In case of etched film, the gold appeared to be conglomerated into spherical particles, which were often observed with microscope.

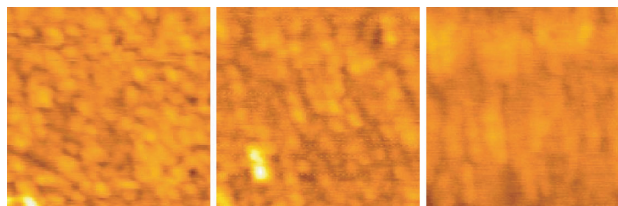In summary, we found that the surface morphology of gold thin film evolved and eventually film was etched away when exposed to UV in chlorine-based liquid. We attributed these phenomena to the photoactivated reaction of gold and chlorine in gold/liquid interface. These effects should be considered when one uses UV in chlorine-based liquids either for photoprocessing or for optical characterization such as spectroscopic ellipsometry or UV–vis spectrophotometry.

Figure 4. AFM images ($0.5 \times 0.5\,\mu$m) of gold surface after 10, 20, and 30 min into UV exposure (from left).

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