Controlled Assembly of Patterned Gold Thin Films Using Photolithographed Self-assembled Monolayers as Templates

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Patterned colloidal Au films were assembled from aqueous solution onto photolithographed self-assembled monolayers of (3-mercaptopropyl) trimethoxysilane films on silica. The colloidal Au closely replicated the mask patterns. The self-assembly were through Au-S covalent bounding. The present approach may be applicable to assembly of microelectronic circuits and microbiosensors.

Organic molecules containing thiol groups(-SH) can be spontaneously adsorbed on Au surface to form well organized self-assembled monolayers(SAMs). In 1983, Nuzzo and Allara first reported the self-assembly of dialkyldisulfides on Au surfaces.[1] Since then, many researches have been carried out on the self-assembly of alkanethiols on Au surfaces.[2] In recent years, the reverse process, i.e., the self-assembly of colloidal Au onto a specially terminated organic surface, has been achieved through specific interaction between the Au nanoparticles and the surface terminating groups like -SH, $-NH_2$, and -CN, leading to a two-dimensional array of Au nanoparticles.[3-6] In another aspect, photolithographic patterning of SAMs attracts considerable interests. Advances in this area include association of biomaterials to and selective metallization of the photolithographed SAMs.[7-11] Here we report a new approach to the metallization of the photolithographed SAMs, which is achieved through covalent bonding of Au colloids to the photolithographed SAMs of (3-mercaptopropyl) trimethoxysilane (MTS).

The substrate was a silica (SiO_2, 300 nm)-coated single crystal silicon wafer. Prior to use, the substrate was immersed in chromic acid at 80 ℃ for 5 h, thoroughly rinsed with deionized, twice-distilled water, ultrasonicated in water for 40 min, dried at 200 ℃ for 2 h. Self-assembly was carried out by immersing the cleaned substrate into a dehydrated benzene solution containing 1×10^{-5} mol·dm^{-3} of MTS for 6h at room temperature. The MTS-coated substrate were irradiated with 253.7 nm UV light produced from an ZSZ30 type ultraviolet light source. The light intensity was 100 μW/cm^2. Two kinds of masks were used. One was transmission electron microscopic (TEM) copper grid and the other was a chromium mask possessing integrated circuit patterns of vertical diffusion metal-oxide-semiconductor (VDMOS) terminal arrays. The chromium patterns were formed on quartz glass slide. Patterned Au films were fabricated by immersing the photolithographed substrate into Au colloid solutions. The Au colloids were prepared according to the reported method with slight modifications.[12] When 500 ml of 0.03% $HAuClO_4$ aqueous solution was heated to boiling, 12.5 ml of 1% trisodium citrate aqueous solution was added. The mixed solution was boiled 10 min. The resulting solution of colloidal Au was characterized by an absorption maximum at 522 nm. Transmission electron microscopic (TEM) observation indicated an average size of 18 nm of Au nanoparticles.

Scanning electron microscopic (SEM) images were obtained on a Hitachi X-650 Scanning electron microscope operated at 20 kV. X-ray photoelectron spectrum (XPS) was recorded on a Perkin-Elmer PHI5300 ESCA spectrometer using a Mg Kα source run at 250 W. The binding energy scale was calibrated to 285.0 eV for the C_{1s} (C-C) feature and a photoelectron take-off angle of 45° was employed. The operating pressure was less than 10^{-8} Torr.

Figure 1 shows the SEM images of the patterned colloidal Au film assembled onto the photolithographed MTS monolayers using two different Cu masks. As can be seen from Fig.1, the colloidal Au closely replicated the patterns of the Cu grid masks.

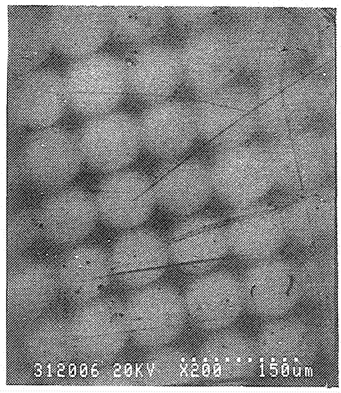

Figure 1. Scanning electron microscopic images of patterned colloidal Au films on MTS monolayer-coated silicon substrates using two different TEM Cu masks.

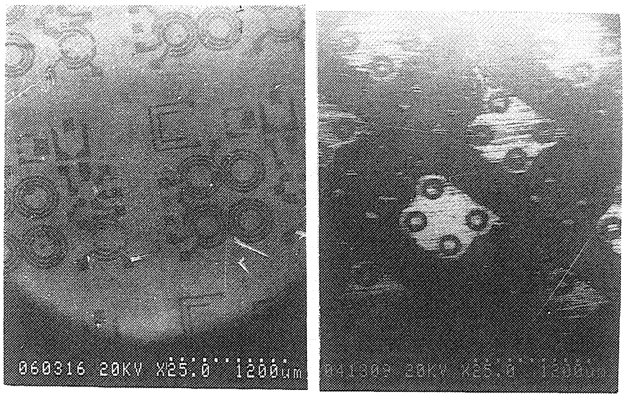

Figure 2. Scanning electron microscopic images of patterned colloidal Au films on MTS monolayer-coated silicon substrates using two Cr masks with VDMOS diffusion terminal array patterns of integrated circuit.

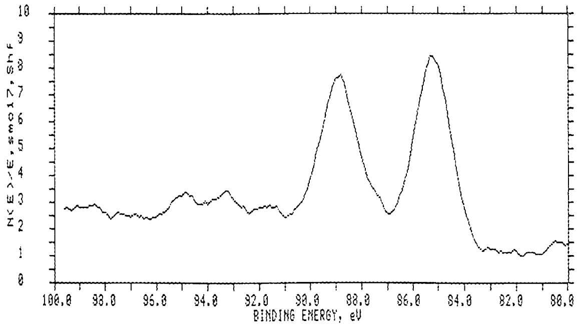

Figure 3. High resolution x-ray photoelectron spectra analysis of Colloidal Au assembled on unirradiated MTS monolayers.

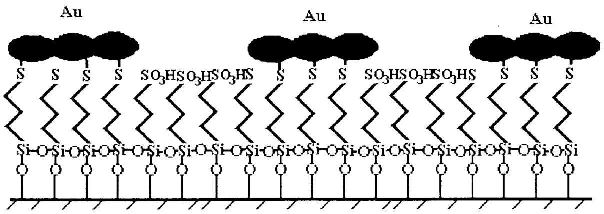

Figure 4. Schematic representation of self-assembly of patterned colloidal Au films on photolithographed MTS monolayers.

The dark and light areas correspond to the areas of colloidal Au films and the photolized regions of the MTS monolayer. Figure 2 shows the SEM images of two VDMOS terminal array patterns of Au colloids on the photolithographed MTS monolayers. Fig.3 shows the XPS spectra of the unirradiated MTS monolayers after assembly of colloidal Au films. The peak at 88.8 eV is the feature of $Au_{4f5/2}$. The peak at 85.3 eV, the feature of $Au_{4f7/2}$, indicates the formation of Au-S covalent bond between Au and -SH groups.[13] This result demonstrates that the self-assembly of colloidal Au are through Au-S covalent bounding. A schematic representation of the self-assembly of colloidal Au onto the photolithographed MTS monolayers was demonstrated in Figure 4.

In summary, metallization of the photolithographed MTS monolayers were realized through covalent bounding of colloidal Au to the -SH terminal groups of the masked regions. This method is rather simple, and operates at ambient conditions. It may be applicable to fabrication of microelectronic circuit. Besides, colloidal Au can bind a large variety of biomaterials, so the micro-patterned colloidal Au films is also important for fabrication of micro-biosensors.

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