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A Novel Patterning Method of Low-resistivity Metals

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Photocatalytic layers of amorphous TiO_2 and polyvinyl alcohol were used for the patterning of low-resistivity metals such as copper and silver without using high cost materials and equipment.

The ability to generate high-resolution and low-resistivity metal patterns has many useful applications especially in the microelectronics industry.[1–5] Conventional metal-patterning methods require high temperature and vacuum apparatuses. They essentially involve the steps of forming patterns using photoresists and etching for removing the undesired metal. In addition, since these steps further include many substeps, they are unfavorable in terms of manufacturing costs. On the other hand, a few methods for forming metal patterns that do not involve the photoresist process and vacuum deposition have been proposed.[6–9]

Photocatalytic materials of crystalline TiO_2 particles and crystalline ZnO films have been also tried for the metal patterning without the photoresist process.[10–13] In these methods, however, the UV irradiation was carried out in an aqueous metal-plating solution or in methanol vapor. And also metal particles can be easily desorbed from the irradiated parts and readsorbed to the unirradiated parts. Therefore, it was not easy to obtain high-resolution patterns. In this study, we used photocatalytic layers consisting of an amorphous TiO_2 film and a film of water-soluble polyvinyl alcohol (PVA) for the patterning of low-resistivity metals as shown in Figure 1. UV light was applied through a photomask (Figure 2a) to selectively activate the photocatalytic layers coated on the glass substrate. After UV-exposure, the substrate was dipped into an aqueous solution of palladium ions. The PVA film was dissolved in the solution. The activated TiO_2 reduced the palladium ions forming deposits of palladium metal on the exposed regions as shown in Figure 2b. It allows electroless plating of metals such as copper, silver, and nickel selectively on the exposed areas. Nickel patterns are shown in Figure 2c. The nickel patterns showed strong adhesion to the glass substrate and were used as metal electrodes for further electroless plating or electroplating of copper to get thicker copper films as shown in Figure 2d.

A thin film (0.03–0.05 µm) of *n*-butyl polytitanate (Tyzor® BTP, DuPont, 5% in 2-propanol) was deposited on the glass plate by spin-coating and baked in air at 100 °C. XPS spectra of the film showed the typical binding energy (458.8 eV) of TiO_2. The X-ray diffraction patterns indicated that the film was amorphous. The FT-IR spectra did not show any organic groups. Therefore, the film obtained was amorphous TiO_2. When the semiconductor, TiO_2, is illuminated, the electron at the valence band is excited up to the conduction band, with the positive hole being left at the site where the electron is originally captured. PVA layer was used as a hole scavenger. The hole scavengers would suppress the recombination of the excited electron with the positive hole. Therefore, the hole scavengers prolong lifetime of the excited electron and enhance reduction reaction

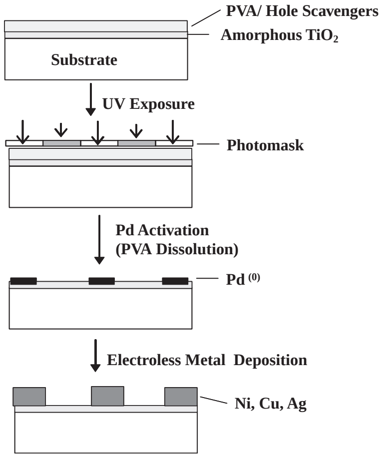

Figure 1. Schematic diagram of a novel metal patterning.

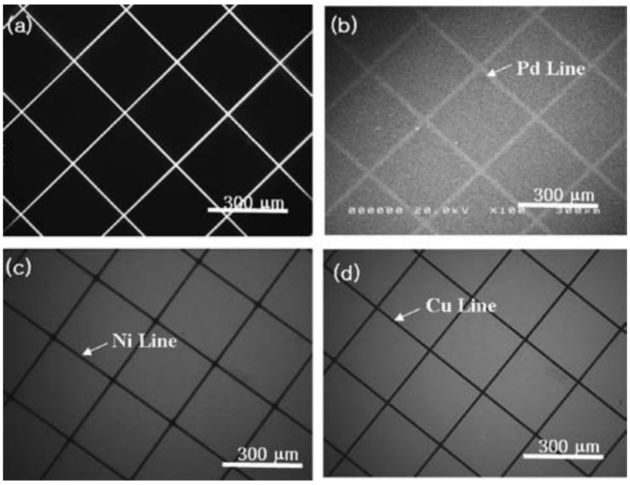

Figure 2. (a) Microscope image of photomask with 10-µm line width. (b) Palladium metal patterns deposited on the exposed parts. (c) Nickel patterns formed by electroless plating. (d) Copper patterns formed by electroless plating on the nickel patterns.

of the metal ion by the excited electron when the excited electron is contact with the metal ion.

Additional hole scavengers, triethanolamine and oxalic acid, were added into the 2.5–5% aqueous solution of PVA (M_r: 6000) to increase the photosensitivity.[10,12] The PVA solution was applied to top of the TiO_2 film and dried at 50 °C. The photonic band gap of the amorphous TiO_2 film coated with the PVA film was 3.95 eV by a UV–vis spectrophotometer. Irradiation by UV light with a wavelength less than 320 nm leads to the generation of electron–hole pairs.

When the power intensity of the UV lamp was $4.5\,\mathrm{mW\,cm^{-2}}$ at 314-nm wavelength, 15 s of exposure time was required to get the nickel patterns of 10-µm resolution and 0.1-µm thickness. Therefore, the photosensitivity was $67.5\,\mathrm{mJ\,cm^{-2}}$. This value is comparable to those ($50–300\,\mathrm{mJ\,cm^{-2}}$) of commercial photoresist systems. The substrate was immersed in an aqueous solution of palladium salt ($PdCl_2$ $0.3\,\mathrm{g{\cdot}L^{-1}}$, KCl $10\,\mathrm{g{\cdot}L^{-1}}$, HCl 10 $\mathrm{mL{\cdot}L^{-1}}$) for 1 min to deposit palladium on the exposed areas of the TiO_2 surface. The photoactivated TiO_2 possesses reducing power for Pd^{2+} ions. However, the reducing power fades away during the storage. For this reason the palladium deposition was carried out right after the UV-exposure. The PVA film was dissolved completely in the aqueous solution of palladium salts and PVA was not detected by FT-IR at all after the treatment. TOF-SIMS image in Figure 3a shows the highly selective deposition of palladium on the exposed TiO_2 areas. In order to get fine patterns which match the photomask, collimated UV light and close contact between the photomask and the photocatalyst layers were adopted. Line width broadening was observed depending upon several factors such as TiO_2 thickness, film baking temperature, and UV exposure energy. This phenomenon is considered to be caused by electron transfer on the TiO_2 layer. Palladium patterns act as catalysts for the following electroless plating of nickel or copper. The composition of the electroless nickel plating solution was $NiCl_2{\cdot}6H_2O$ $10\,\mathrm{g{\cdot}L^{-1}}$, NH_4Cl $40\,\mathrm{g{\cdot}L^{-1}}$, $NaH_2PO_2{\cdot}H_2O$ $30\,\mathrm{g{\cdot}L^{-1}}$, and CH_3COONa $6\,\mathrm{g{\cdot}L^{-1}}$ in water.

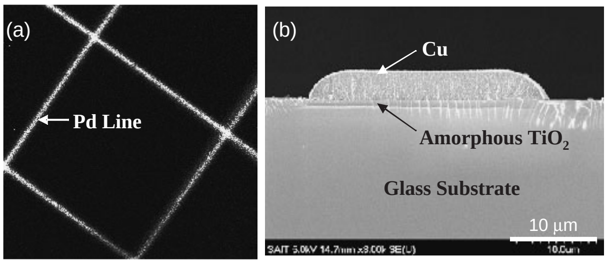

Figure 3. (a) TOF-SIMS image of palladium metal patterns on the exposed parts. (b) Vertical SEM image of the substrate after copper electroplating.

Conventional electroless plating of nickel, copper, and silver can be applied on the palladium metal patterns. Nickel patterns with thickness of 0.3–0.4 µm and resolution of 10 µm could be produced from the selective electroless nickel plating. High resolution patterns of copper and silver were also obtained. However, copper and silver films of the required thickness (more than 0.3 µm for microelectronic device application) could not be deposited by electroless plating. When the thickness of the copper film reached 0.3 µm, peeling of the metal film from the substrate was observed. The silver film was also peeled off when the thickness reached 0.1 µm.

It was investigated whether the copper film thicker than 0.3 µm could be deposited on the nickel patterns of 0.05–0.2 µm-thickness or not. Thermal treatment of nickel films at 250–280 °C yields the strong adhesion to the glass substrate. Selective copper electroless plating could be applied on the isolated nickel metal patterns. Copper films of more than 0.3-µm thickness were obtained on the nickel metal patterns from the copper electroless plating using formaldehyde as a reducing agent. However, the copper films thicker than 1 µm showed poor adhesion to the substrate. In the case of connected metal lines like mesh type patterns, copper electroplating by using nickel patterns as electrodes can be applied to get the thick copper metal patterns. Using the electroplating method, copper patterns of thickness larger than 1 µm on the 0.1 µm-thick nickel patterns were obtained as shown in Figure 3b. Line width broadening was observed as the metal thickness increases. When the photomask with patterns of 10-µm line width was used, the line width of copper patterns became about 20 µm as the thickness reached 3 µm. The copper films prepared by electroless plating or the electroplating showed the low resistivity of less than 3 µΩ·cm. This novel patterning method of copper does not need the metal deposition on the entire area of the substrate and the subsequent patterning processes using expensive photoresists and chemical etchants.

In summary, high resolution patterns of low-resistivity metal were formed at a few process steps using novel photocatalytic layers of amorphous TiO_2 and PVA.

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