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A Novel Method for Low-Resistivity Metal-Interconnection by Using Metallic Functional Liquids and Catalytically Generated Hydrogen Atoms

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ABSTRACT

A novel method to make low-resistivity metal lines in assembled silicon (Si) integrated circuit (IC) chips or other semiconductor chips with high-speed and low-cost is demonstrated. In the method, functional silver (Ag)-liquid (Ag-ink) which contains Ag nanoparticles (NPs) in organic solution is used to draw metal-lines in trenches formed on a plastic substrate by imprint technology. Surface energy of trenches is modified by exposing the substrate to ultra-violet (UV) light with the purpose of concentrating the functional Ag-ink into trenches by capillary effect in order to connect with electrodes of Si chips. The resistivity of such metal-lines can be lowered to 4×10^{-6} Ωcm by exposing the Ag metal-lines to hydrogen (H) atoms generated by catalytic cracking reaction with a heated tungsten catalyzer. X-ray photoelectron spectroscopy (XPS) proves that H atoms can remove organic compounds surrounding Ag NPs, resulting in the low-temperature sintering of NPs as confirmed by scanning electron microscopy (SEM). The method is promising for low-cost fabricating of IC cards or other electronic devices utilizing assemble of many semiconductor chips.

INTRODUCTION

Low temperature formation of low-resistivity metal-lines with high speed has collected attentions for forming metal-interconnection in the assembling process of electronic devices such as IC-chips. It can be used for making IC cards, and also, it can be used in metal-line formation among many light-emitting diode (LED) chips delivered at pixel positions in large area LED displays. In addition, the metal interconnection is also significant in a rising technology for the fabrication of ultra-large flat panel displays (FPD) such as liquid crystal display (LCD) or organic LED (OLED) display in which millions of Si IC chips embedded at pixel positions control the pixels instead of conventional thin film transistors.

We have investigated the formation of metal lines at trenches on a plastic substrate by using metallic functional liquid containing metal NPs dispersed in an organic solvent [1]. In particular, Ag NPs are used due to their specific advantages such as high electrical conductivity and chemical durability [2,3]. The metallic functional liquid is concentrated inside trenches for forming metal lines by covering the substrate with a hydrophobic polytetrafluoroethylene (PTFE) film and converting only trench surface to hydrophilic by ultra-violet (UV) light irradiation. However, the Ag lines obtained after drying at 40 ^{o}C have a high electrical resistivity due to remaining organic compounds in the lines. As a novel solution to lower the resistivity, hydrogen (H) atoms generated catalytically from hydrogen molecules in a catalytic chemical vapor deposition (Cat-CVD) system are used to remove organic compounds. The Ag lines with an electrical resistivity of 4×10^{-6} Ωcm, which is comparable to that of the metal lines formed by vacuum evaporation, have been achieved.

The present paper demonstrates the novel technology to form low-resistivity metal lines for metal-interconnection by using metal-ink and also a new tool for printing electronics or related process using functional liquid.

EXPERIMENTAL PROCEDURE

At first, a mold of crystalline silicon (c-Si) was made by Bosch etching process (Sumitomo MUC21 RD). This c-Si mold was imprinted onto a 200 µm-thick cyclo-olefin polymer (COP) substrate, named "Zeonor" produced by Nippon Zeon Corporation, to form trenches which are used for formation of metal lines. In order to concentrate the functional liquid into such trenches, the COP substrate was covered with a hydrophobic PTFE thin film prepared by Cat-CVD method before the imprinting process. After imprinting, the surface of trenches became partially hydrophilic due to the removal of PTFE at the trenches. The plastic substrate was subsequently exposed to UV light from a mercury lamp at a wavelength of 251 nm and an irradiance of 15 mW/cm^2 to improve the hydrophilicity of the trench surface. The Ag lines were formed by dropping the Ag functional liquid, which contains Ag NPs dispersed in 1,3-propanediol and water as solvent, on substrates. Because of the hydrophobic property of the substrate surface and hydrophilic property in trenches, the dropped liquid is likely to concentrate inside trenches to form metal lines there.

Next, the metal lines were dried at 40 ^oC, and then, the electrical resistivity of the Ag lines was lowered by treatment with H atoms generated in a Cat-CVD system. The temperature of a tungsten (W) catalyzer for generating H atoms by catalytic reaction was set at 1350 ^oC and the processing time was fixed at 25 min. Gas pressure during H treatment was 70-100 Pa, and the substrate temperature was ~100 °C. The image of a sample after H treatment is shown in Fig. 1.

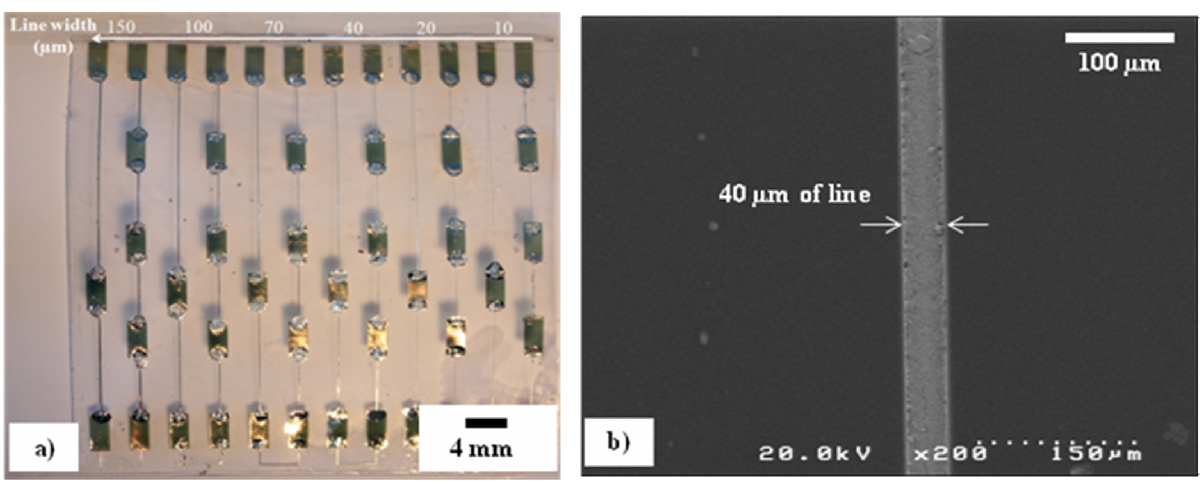

Figure 1. The photograph of Ag lines connecting to Au electrodes on a CPO substrate with various widths from 10 to 150 µm (a) and the SEM image of a 40 µm-wide Ag metal line after H treatment (b).

In the study, gold electrodes were fabricated by vacuum evaporation at the pit positions to support the electrical measurement. The electrical resistivity of the Ag lines was measured by four point probe technique. The micro-structural morphology of the Ag lines was observed in a SEM (Hitachi S-4100). For analyzing the composition of metal lines, XPS (ESCA-5600) with a monochromatized Al K_α source (1486.6 eV) operated at 13.9 kV was used. Contact angle (CA) of water droplets was measured on Drop Master DM 300 of Kyowa Interface Science Co.

EXPERIMENTAL RESULTS

Capillary phenomena in forming metal lines

When the Ag functional liquid was dropped on a blank COP substrate, it overflows and covers all of substrate surface because the COP substrate is quite hydrophilic. In order to concentrate the functional liquid only inside the trenches, the COP substrate was covered with a hydrophobic PTFE film before mold-imprinting, as mentioned above. The high CA between a water droplet and the PTFE-covered COP substrate (137^o) shown in Fig. 2 indicates a high hydrophobicity of the PTFE-covered substrate. With appearance of a PTFE film, the functional liquid did not overflow anymore. However, the functional liquid could not automatically fill in the trenches, though PTFE film at trench positions is expected to be damaged, and then partially removed by the Si mold. A simple process for surface modification of a plastic substrate due to exposure of UV light has been applied to improve hydrophilicity of the trench surface. During UV treatment, C-C bonds in COP were oxidized by ozone, which was generated under UV light, to form hydrophilic groups such as -C-OH, -C=O, and -COOH [4], resulting in a significant decrease in CA between a water droplet and the modified COP substrate from 86^o for the non-modified COP to ~20^o for COPs after UV irradiation for 3 min or more (Fig. 2). On the other hand, the CA between the water droplet and the PTFE-covered COP substrates does not decrease significantly (Fig. 2) due to stability of PTFE. Consequently, the functional liquid did not overflow on modified PTFE-covered substrate and automatically filled in trenches for the metal line.

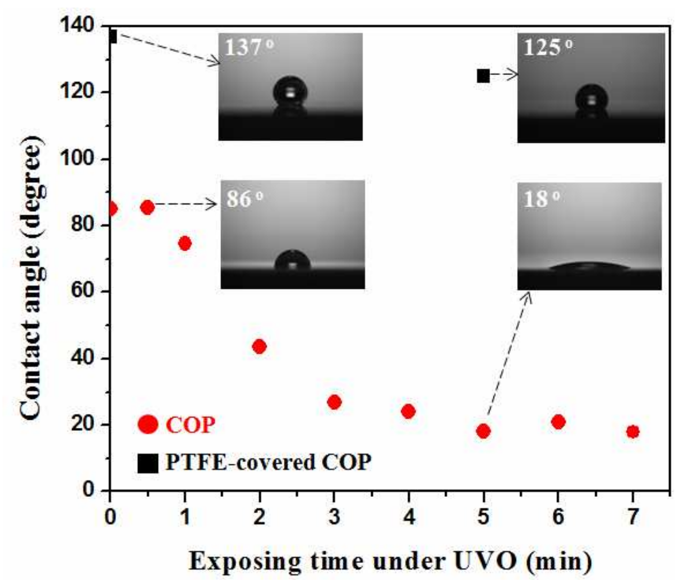

Figure 2. Dependence of the CA between a water drop and the UV-treated COP substrate on the exposing time.

Hydrogen treatment for lowering metal line resistivity

The Ag lines formed after drying at 40 °C have high electrical resistivity of about 10^{-2} Ωcm, which does not satisfy realistic applications. The high electrical resistivity of the Ag lines is mainly due to remaining organic compounds surrounding Ag NPs, indicated by the existing of the C1s peak in the XPS spectra (Fig.4, black line). The organic layer among the NPs not only plays a role of an insulating layer but also prevents the NPs to sinter with each other. Organic compounds in a metallic film are conventionally removed by thermal annealing at high temperature under air. In this study, however, the COP plastic substrate is applied aiming at the applications in flexible electronic devices, thus a high temperature annealing cannot be used.

A novel method for the low-temperature removal of organic components has been developed in our group. That is, the organic compounds are effectively removed at moderate annealing temperatures around 100 °C by H atoms generated by the catalytic cracking of H_2 gas with a heated W catalyzer in a Cat-CVD apparatus [5]. Figure 3 shows the SEM plan views of Ag lines before and after the H annealing. Before the annealing, the Ag NPs with a size of *ca.* 20 nm were individual particles (Fig. 3a). After the Ag lines were exposed to H atoms, the organic components were converted to small and volatile compounds, which were quickly removed from the metal-lines into vacuum, as being shown by disappearance of C1s peak in XPS spectrum (Fig. 4, red line). The removal of organic compounds by H atoms enables the Ag NPs to sinter with each other. The formation of necks and sintering between Ag NPs can be clearly seen after 10-min H annealing (Fig. 3c,d). The thickness of the Ag lines decreased from 1.6 μm before annealing to 1.0 μm after 25-min annealing, as can be seen in the cross-sectional view images in Fig. 3e and Fig. 3f, respectively. The removal of organic compounds and the sintering of Ag NPs result in a significant diminish of the electrical resistivity of the Ag lines to 4×10^{-6} Ωcm, being suitable for various applications.

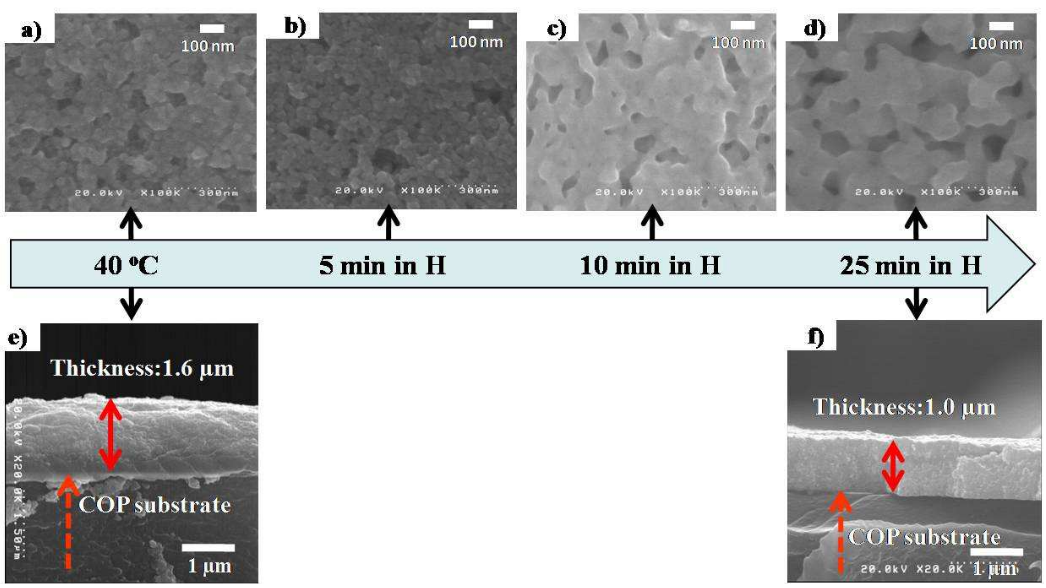

Figure 3. The plan view SEM images of Ag lines after drying at 40 °C (a), and subsequently annealing at 100 °C under H atoms for 5, 10, 25 min (b, c, d, respectively). The cross-sectional SEM images for the Ag lines after drying at 40 °C (e), and subsequently annealing under H atoms for 25 min (f).

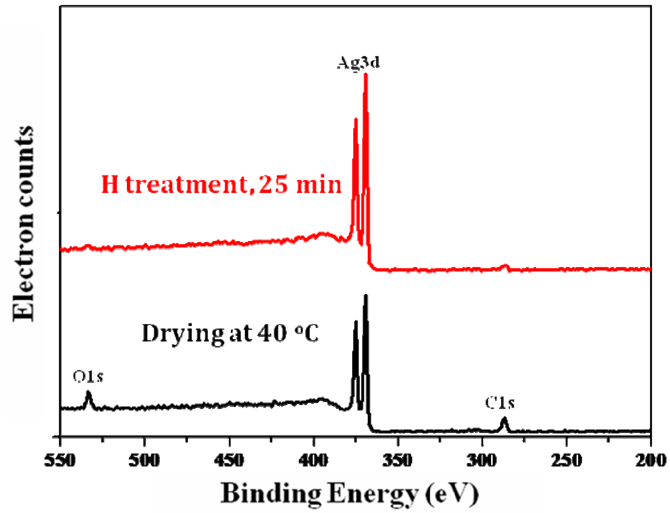

Figure 4. XPS spectra of Ag films after being dried at 40 °C (black), and subsequently annealed under H atoms for 25 min (red).

DISCUSSION

The Ag functional liquid dropped on the blank COP substrate overflows the surface due to the compatibility between the substrate and the organic solvents in the ink. After the COP substrate being covered with the hydrophobic PTFE film, the dropped Ag ink kept its shape, and therefore could not fill in the trenches automatically. The fact indicates that some of PTFE still remained inside the trenches even after imprint. However, Ag ink is automatically filled in the trenches subsequent to UV treatment of pattern, despite the fact that the surface properties of the PTFE-covered COP substrate were scarcely affected by the UV treatment as shown in Fig. 2. This seemly contradicting phenomenon could be explained by the fact that, during mold-imprinting on the PTFE-covered COP substrate, the thin PTFE film has been cut and/or stressed by the c-Si mold, thus the PTFE did not cover the trench surface completely, especially on the trench walls. As a result, ozone generated under UV light can modify the trench surface, enabling the capillary flow to occur.

It has been reported that photo-resist usually comprised of organic compounds can be easily removed by H atoms in making volatile C_nH_m (n and m are integers) species [5]. This discovery was utilized to lower resistivity of the metal lines prepared from functional liquid including organic compounds. Figure 4 shows the removal of organic compounds from the Ag lines after 25-min H annealing indicated by an almost complete disappearance of a C1s peak in the XPS spectrum (black line). Figure 3 demonstrates that Ag NPs remaining after removing organic solvent are likely to sinter and even particle size appears to increase. This means that, apart from the simple removal of organic compounds in Ag lines, other additional effects also occurs as a result of the H treatment. X-ray diffraction (XRD) measurement confirms the increase of grain size from the decrease of a diffraction peak width. The surface and boundary diffusion during the sintering of the Ag NPs may be the reason for the particle enlargement [6].

One might doubt that the electrical resistivity of the prepared Ag line is still higher than that of the bulk Ag (4.0×10^{-6} Ωcm comparing with 1.6×10^{-6} Ωcm). However, if we account for the pores existing in the Ag lines as being seen in Fig. 3d, the electrical resistivity of the Ag lines could be in the level of that of the bulk Ag.

CONCLUSIONS

The study presents the feasibility of a simple and high-speed method for making metal lines on a CPO plastic substrate toward wide applications in flexible electronic device production. The Ag lines with various widths of 10-150 μm have been formed precisely at their desired positions by covering the COP substrate with the hydrophobic PTFE film and modifying trench surface by UV light. The electrical resistivity of Ag lines was reduced to the level of bulk Ag by the H annealing at about 100 ^{o}C. The success of this work has a high potential for future development of flexible and printing electronics.

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