Title	Novel technique for formation of metal lines by functional liquid containing metal nanoparticles and reduction of their resistivity by hydrogen treatment
Author(s)	Nguyen, Thi Thanh Kieu; Ondaira, Keisuke; Shimoda, Tatsuya; Matsumura, Hideki
Citation	Journal of Vacuum Science and Technology B, 28(4): 775-782
Issue Date	2010-07-07
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/9525
Rights	Copyright 2010 American Vacuum Society. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Vacuum Society. The following article appeared in Nguyen Thi Thanh Kieu, Keisuke Ondaira, Tatsuya Shimoda, and Hideki Matsumura, Journal of Vacuum Science and Technology B, 28(4), 775-782 (2010) and may be found at http://dx.doi.org/10.1116/1.3456179
Description	

Novel technique for formation of metal lines by functional liquid containing metal nanoparticles and reduction of their resistivity by hydrogen treatment

Nguyen Thi Thanh Kieu[a)]
Japan Advanced Institute of Science and Technology (JAIST), Asahidai, Nomi-shi, Ishikawa-ken 923-1292, Japan and Institute of Physics Ho Chi Minh City, No. 1, Mac Dinh Chi, District 1, Ho Chi Minh City, Vietnam

Keisuke Ohdaira, Tatsuya Shimoda, and Hideki Matsumura
Japan Advanced Institute of Science and Technology (JAIST), Asahidai, Nomi-shi, Ishikawa-ken 923-1292, Japan

A novel technique for formation of metal lines for electronic devices, and for reduction of resistivity in such metal lines, is proposed. In the technique, the metal lines are formed in trenches by using functional liquids containing metal nanoparticles. The trenches are constructed on a plastic substrate by imprint of a patterned mold. When the whole surface of the plastic substrate is covered with a hydrophobic film, the hydrophobic property disappears only in the trenches due to the pressing process of the imprint, and thus the functional liquid automatically accumulates into the trenches. When the metallic functional liquid is modified with tween-20 (polyoxyethylene-20), metal lines with a width of 10 μm are formed by capillary effect. The resistivity of such metal lines can be lowered to the order of 10^{-6} Ω cm by exposing them to hydrogen atoms generated in vacuum by catalytic cracking of hydrogen molecules with heated tungsten wires. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3456179]

I. INTRODUCTION

Formation of patterned metal lines with low resistivity is one of the key processes in fabricating integrated electronic devices. The deposition of metal film and successive lithographic processes are commonly used for formation of metal lines with widths less than 1 μm. For lines with widths larger than several 10 μm, screen-printing or other printing technologies are widely used, although bumps sometimes appear in solidified metal lines. However, if low-resistivity metal lines with widths from 10 to several 10 μm can be formed with precise patterns but without particular bumps, such metal lines can be used in fabricating integrated circuit (IC) cards, light emitting diode displays, or other devices.

One of the authors has developed a new method to fabricate a pixel-controlling substrate of liquid crystal display, in which on-off and brightness of pixels are controlled by millions of IC chips instead of the conventional amorphous-silicon (*a*-Si) thin film transistors.[1,2] For this system, after millions of small-size IC chips are deposited in the positions of pixels, such IC chips should be quickly connected with low-resistivity metal lines, but without using any expensive tools. In addition, the metal lines should be formed exactly at the position of the electrodes on IC chips. That is, the metal lines are required to be automatically formed with IC chip deposition in a self-aligned manner.

For these future applications, we proposed a novel technique to make low-resistivity metal lines without bumps or particular structures. In the technique, the metal lines are made inside the trenches by using functional liquid containing metal nanoparticles, so-called metal ink. The trenches are constructed on a plastic substrate by an imprint technology using a patterned mold. When the plastic substrate is covered with hydrophobic thin films in advance, the functional liquid dropped onto the whole surface of the substrate is likely to flow on substrate surface and finally accumulates automatically into the trenches to form metal lines there, since the hydrophobic property disappears only in the trenches due to the pressure of imprinting. The advantage of this method is that the metal lines can be formed to contact the electrodes on IC chips in a self-aligned manner if such IC chips are embedded into the plastic substrate at the same time when the trenches are formed. Recently, Frey *et al.*[3] developed the method of patterning metal lines on a polymeric substrate. However, this process is still complicated and the electrical characterizations of metal lines are not mentioned.

In this technique, the development of methods to make uniform metal lines inside narrow trenches and to lower the resistivity of such metal lines is one of the most important issues. In the present article, we studied the effect of addition of surfactant, tween-20 (polyoxyethylene-20: $C_{18}H_{114}O_{26}$), onto functional liquids, and found that metal lines with a width of 10 μm are easily formed in the trenches by capillary effect. We also studied the method to reduce the resistivity of metal lines, and found that the resistivity of metal lines made from functional liquid can be lowered to the order of 10^{-6} Ω cm by exposing them to hydrogen (H) atoms generated in vacuum by catalytic cracking of hydrogen molecules (H_2) with heated tungsten (W) catalyzer.
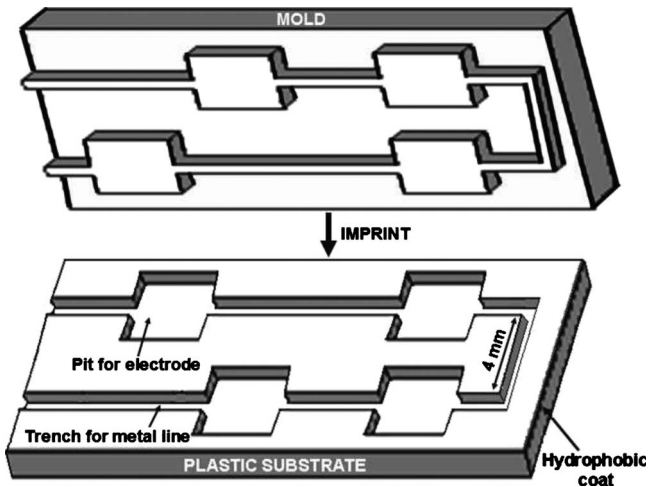
a)Electronic mail: kieu-ntt@jaist.ac.jp

FIG. 1. Fundamental model of proposed idea for metal interconnections.

FIG. 2. Present procedure of the metal-interconnection process.

The development of low-resistivity and stable contacts among such metal lines and electrodes on IC chips is another important issue. Actually, we have succeeded in forming low-resistivity Ohmic contacts between gold electrodes and the present metal lines. However, here, we concentrate on demonstrating the validity of the fundamental concept of this newly proposed technique to form metal lines and to reduce their resistivity.

II. OUTLINE OF PROPOSED TECHNIQUE AND EXPERIMENT

A. Outline of technique

The fundamental idea or concept of the proposed technique to form low-resistivity metal lines is explained as follows.

First, a mold with patterns of both trenches and pits is prepared. Second, the mold is used to make trenches and pits by pressing it onto a plastic substrate. The pits are used to make metal contact area, and the trenches are used to form the metal lines. Here, the whole surface of the plastic substrate is covered with a hydrophobic thin film before pressing. Third, metallic functional liquid including metal nanoparticles is dropped onto the substrate. The liquid flows on the hydrophobic surface and accumulates only inside the trenches. Fourth, the metal lines made from metallic functional liquid are dried to evaporate solvent, and they are put into a vacuum chamber for expose to H atoms. By this process, the solvent of the functional liquid is removed completely, and the resistivity of the metal lines can be significantly lowered.

The mold with patterns used in the present experiment and imprint process itself are schematically illustrated in Fig. 1. The figure shows the trenches and pits on the plastic substrate made by imprinting of the patterned mold. In the present experiment, the contacts between the electrodes on IC chips and metal lines are not particularly studied. However, if the IC chips are embedded in the positions of pits and the electrodes on the IC chips are located in the areas touch-
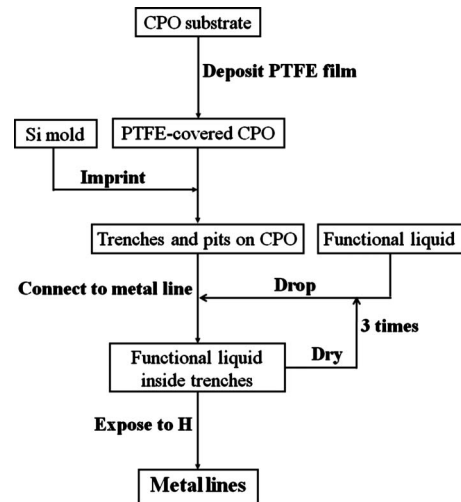
ing the ends of metal lines, self-aligned formation of metal-interconnection among the electrodes of IC chips and metal lines can be theoretically expected.

B. Experimental procedure

The experimental procedure is briefly summarized in Fig. 2.

First of all, the mold was made by sculpturing a crystalline silicon (Si) wafer. To obtain sharp edges at the walls of mold patterns, Bosch etching process[4] using the apparatus, Sumitomo MUC21 RD, was applied with C_4H_8 and SF_6 gases in inductive coupled plasma. The etched depth, which was equal to the height of trench-patterns, was about 20 μm. Various trenches with widths from 10 to 150 μm, and lengths from 6 to 20 mm, were formed. Every 6–20 mm along the lengths of trenches, pit areas of 1.5×3 mm^2 were formed for contact-electrodes, as shown in Fig. 1. The difference between designed width and actual width of trench-patterns after Bosch etching was only 0.5 μm, even for the narrowest pattern of 10 μm width. The error of pattern size was only 5 % in the Bosch etching process.

After making the mold, the patterns in the mold were imprinted on a 200-μm-thick cyclic polyolefin (CPO) substrate, namely, "Zeonor" by Nippon Zeon Co. Here, Zeonor with a softening temperature of about 163 °C was used. The substrate was covered with a hydrophobic thin film of polytetrafluoroethylene (PTFE), "Teflon" by its commercial name. The PTFE film was prepared at room temperature by catalytic chemical vapor deposition (Cat-CVD), often called "Hot-Wire CVD," with hexafluoropropylene-oxide (HFPO) gas as a source gas. The deposition conditions are described in the next paragraph. The hydrophobic properties were studied by measuring the contact angle of a droplet of liquid. The contact angle between the droplet and the substrate was measured by contact angle measurement apparatus, Drop-Master DM 300 of Kyowa Interface Science Co.

There are several reasons for using CPO substrate as the plastic substrate.[5] It is resistive to all chemicals used in the

fabrication process of devices or displays, and also flexible and fluidic, keeping precise positional accuracy during imprint when the temperature is moderately elevated.[6] The imprint was carried out by elevating the temperature of the CPO substrates, covered with PTFE thin films in advance, to about 170 °C. The ramping rate was about 2.3 °C/min and kept at 170 °C for about 30 min during pressing of the mold. Later, the temperature was gradually lowered at a dumping rate of 3 °C/min down to 120 °C, while keeping the mold pressed onto the substrate. The average pressure was 8.6 MPa. After the temperature was lowered below 120 °C, the pressing was stopped and the mold was separated from the substrate. It is generally known that separation after imprint is often not so easy. However, probably because the surface was covered with PTFE film, the separation could be performed without any particular difficulties.

The time required for this process is about 1 h in total. However, if we press many substrates at the same time by piling them up, the average time for imprinting one substrate may be reduced to a few minutes.

After dropping metallic functional liquid and forming metal lines, the resistance of the metal lines was measured by using a precision semiconductor parameter analyzer, Hewlett Packard, HP 4156, with a metal-shielded box. The measurement was carried out by two-point probes at room temperature with applied voltages from −1 to 1 V, and then the resistivity of Ag lines was calculated using the following equation:

$$\rho = \frac{Rtw}{l}, \tag{1}$$

where ρ is the resistivity of a Ag line (Ω cm), R is the resistance of a Ag line (Ω), t is the thickness of a Ag line (cm), w is the width of a Ag line (cm), and l is the length of a Ag line (cm). Here, w and l were obtained from the designed pattern, and t was determined by scanning electron microscopy (SEM) images.

Since we used two-point probe technique, one may worry about the influence of the contact resistance between measuring probes and measured metal lines. However, as shown later, the measured resistivity is on the order of 10^{-6} Ω cm, even if the contact resistance among measuring probes and the metal lines is included. The microstructural morphology of the metal line surface was observed by optical microscopy, using Olympus BX51, and a scanning electron microscope, Hitachi S-4100. To analyze the organic compounds existing in the metal lines, the Ag functional liquid was dropped on floating-zone grown crystalline Si wafers with a resistivity of more than 1000 Ω cm, and then was treated similarly to the metal line forming process. The infrared (IR) absorption spectra were taken by a Fourier transform infrared (FT-IR) spectrophotometer, Shimadzu-8300, in a transmission mode.

TABLE I. Conditions for deposition of PTFE film by Cat-CVD.

Deposition time	10 min
Film thickness	200 nm
Catalyzer material	W
Source gas	HFPO
Deposition pressure	65 Pa
Temperature of catalyzer (T_{cat})	750 °C
Distance between substrate and catalyzer (D_{cs})	12 cm

III. FUNDAMENTAL PROCESS STEPS FOR METAL LINE FORMATION

A. Preparation of hydrophobic thin film by Cat-CVD

The synthesis of PTFE hydrophobic thin films by Cat-CVD was reported in our previous paper.[7] Deposition conditions used in this research are summarized in Table I. In general, PTFE films are obtained with deposition rates from 100 to 500 nm/min by using metal wires containing nickel as a catalyzer. However, in this experiment, to reduce the deposition rate, tungsten (W) was particularly used as a catalyzer. The deposition rate less than 50 nm/min was realized in this case, and the thickness of PTFE films was usually kept at about 200 nm.

At the moment, we have not attempted to use PTFE films prepared simply by spraying of liquid, because sprayed PTFE film has to be annealed after deposition and the thickness control is not so accurate. Although we do not neglect the possibility of using such PTFE films in future, Cat-CVD films are apparently superior for controlling the thickness and quality of films at room temperature.

B. Formation of metal lines by using metallic functional liquid

The key material for this technique is metallic functional liquid including metal nanoparticles. In this experiment, as a functional liquid, metallic functional ink containing 40 nm size silver (Ag) nanoparticles was used. The Ag nanoink was diluted by 1,3-propanediol $[CH_2(CH_2OH)_2]$ and pure water with volume ratios of 1:2.5:2.5, respectively. Various factors should be taken into account to form metal lines, for instance, the evaporation rate of solvents, the density of metal nanoparticles, and the contact angle between a droplet of functional liquid and substrate are all key factors.

In addition, the capillary effect inside the trench is the most important phenomenon in forming metal lines with narrow widths. In the original functional liquid, such capillary effect could not be observed because of large contact angle between the liquid and substrate in the trench. Thus, the tween-20 surfactant was added to the liquid to adjust the contact angle between functional liquid and the substrate surface in trenches.

Figure 3 shows the photographs of a droplet on the CPO substrate covered with PTFE film and the plane view of the trench near large pits for electrodes. Figures 3(a)–3(c) show the photographs of the modified functional liquids with volume ratios (VRs) of tween-20 to original functional liquid of
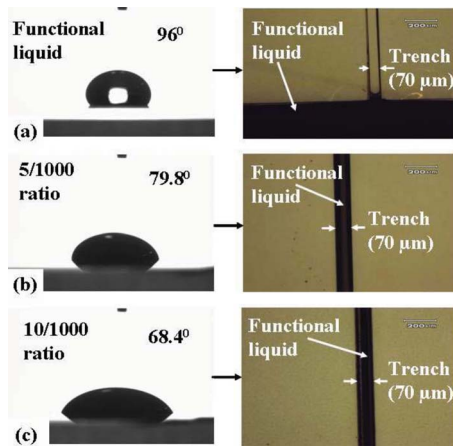
FIG. 3. (Color online) Contact angle of Ag functional liquid on a PTFE-covered CPO substrate (left) and behavior of the functional liquid inside trenches with (a) original functional liquid, (b) 5/1000 VR of surfactant, and (c) 10/1000 VR of surfactant. The contact angles are observed from glancing direction.

0, 5/1000, and 10/1000, respectively. The width of the trench was 70 μm. It is demonstrated that the dropped functional liquid without tween-20 accumulated only in the pits for electrodes, and could not penetrate into trenches, even wide trench of 70 μm width. The liquid could penetrate inside the trench only when VR exceeded 5/1000. Although the photographs are shown for lines with width of 70 μm, the penetration of the liquid into the 10-μm-wide trench is completed for VR over 5/1000, as demonstrated later in Fig. 5(a).

Figure 4 shows the contact angles of the droplet of functional liquid with various VRs on both PTFE-covered CPO substrate and bare CPO substrate. The contact angles are decreased by adding tween-20. However, there is still a difference in the contact angles on the two substrates for various VRs. It is revealed that this difference plays a role in the droplet moving from the PTFE-covered surface into the trenches, where the hydrophobic property of PTFE film or PTFE film itself may be broken during pressing.
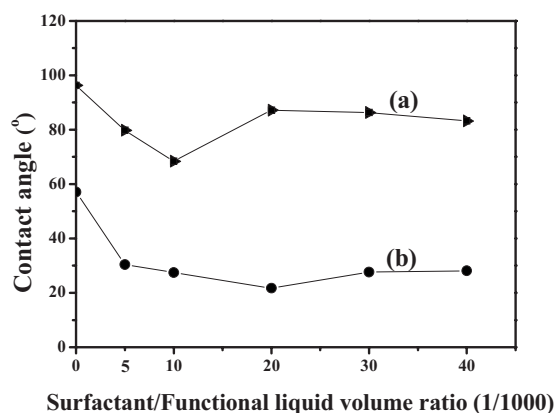

FIG. 4. Dependence of contact angles on the volume ratio of surfactant to original functional liquid, for (a) on PTFE-covered CPO substrates and (b) on pure CPO substrates.
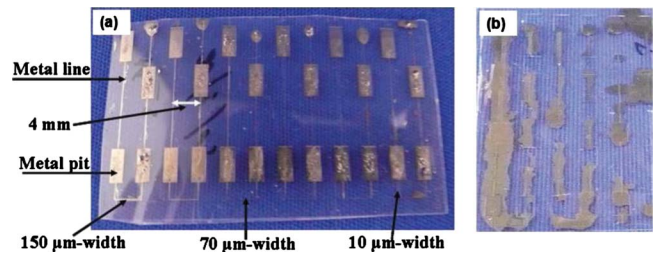

FIG. 5. (Color online) Photographs of the CPO substrate after dropping functional liquid (a) covered with PTFE film and (b) without PTFE film.

Figure 5(a) shows the photograph of an experimental CPO substrate in which the liquid accumulates only in the trenches and pits (liquid VR of 5/1000). The patterns of trenches with various widths from 10 to 150 μm were used in the present experiment, as mentioned already. The distance between two parallel trenches was kept at 4 mm. Figure 5(b) also shows a similar photograph, after dropping the same functional liquid onto the CPO substrate without a covering of PTFE film. From the figure, it is confirmed that the liquid can be seen only in the trenches with widths from 10 to 150 μm s and in the pits for PTFE-covered CPO substrate, although the liquid appears to overflow from the trenches when the substrates are not covered with PTFE films and then when there is no difference of contact angles at between the trenches and the substrate surface.

C. Lowering of resistivity of metal lines

The last process, another important step, is a treatment for metal lines to reduce their resistivity. The annealing of the metal lines is required to evaporate the solvent and surfactant in the functional liquid, since they may restrict electronic conduction. A suitable solution was to apply the process using H atoms generated in catalytic cracking reaction of H_2 gas with heated W wires in Cat-CVD system.[8]

After dropping, the liquid accumulated into the trenches to form the metal lines, and these metal lines were soft annealed at 40 °C in air to dry them up. The procedure of dropping liquid and successive drying was repeated three times to form metal lines with suitable thickness over 1 μm, as indicated in Fig. 2.

According to data reported by the author's group,[9] the density of H atoms can be controlled from 10^{10} to 10^{14} cm^{-3} by changing the temperature of W catalyzer (T_{cat}) from 1100 to 1750 °C. It is known that H atoms are likely to react with carbon (C) and other elements to remove them from the metal lines by making compounds with such elements. Actually, the photoresist, which consists of compounds related to C atoms, can be successfully removed at rates around several μm/min by H atoms generated in the Cat-CVD apparatus.[10]

In the present experiments, T_{cat} was elevated from 1150 to 1350 °C and the processing time was varied from 5 to 90 min. Gas pressure during H treatment was about 70–100 Pa. The Cat-CVD apparatus was carefully cleaned and was used for H atom generation. The resistivity of the metal lines with
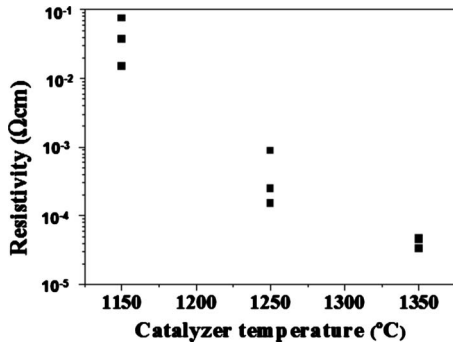
FIG. 6. Resistivity of metal lines as a function of T_{cat} in H treatment with a gas pressure of 70 Pa.

FIG. 8. FT-IR spectra of (a) Ag film formed by drying a drop of Ag functional liquid (without tween-20) at 40 °C, (b) Ag functional liquid with tween-20, (c) Ag film formed by drying a drop of tween-20-added Ag functional liquid at 40 °C, and (d) Ag film formed similar with (c) then treated by H atoms.

a width of 70 μm is plotted in Fig. 6 as a function of T_{cat}. By elevating T_{cat} from 1150 to 1350 °C, the resistivity was decreased from 10^{-2} to 10^{-5} Ω cm. To avoid elevating the substrate temperatures over the softening temperature of substrates due to the thermal radiation from the catalyzer, T_{cat} was fixed at 1350 °C during the atomic H process.

The resistivity is also dependent on the annealing time. However, it is likely to saturate at values of 10^{-5} Ω cm after 25 min H exposure for T_{cat} of 1350 °C, as shown in Fig. 7. It is known that the removal rates of photoresist are depending on both the amounts of H atoms and substrate temperatures.[11] When the substrate temperature is elevated from 100 to 170 °C, the removal rate increases from 0.4 to 1.1 μm/min.[11] For higher substrate temperature, H atoms can have enough times to form C—H related compounds, unless it is not too high to let H atoms desorbing from the resist surface. On the other hand, the density of H atoms itself increases from 10^{11} to 10^{12} cm^{-3}, as T_{cat} is elevated from 1150 to 1350 °C.[9] It is then speculated that the density of H atoms increases enough and the substrate temperature is elevated properly by elevating T_{cat} to 1350 °C for the present system.

By observing IR absorption spectra for the above samples, it is easy to realize the remarkable effect of H atoms. Because Ag functional liquid contains Ag nanoparticles, diluting solvents such as 1,3-propanediol, water, and tween-20 surfactant, the specific peaks for O—H bond at 3600–3200 cm^{-1}, C—H bond at 3000–2850 cm^{-1}, C=O
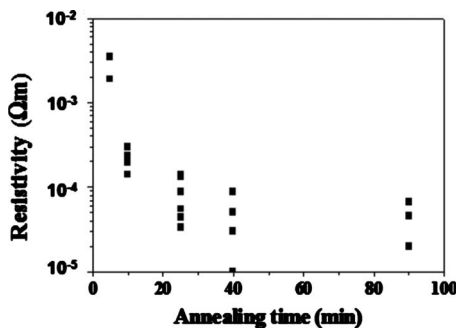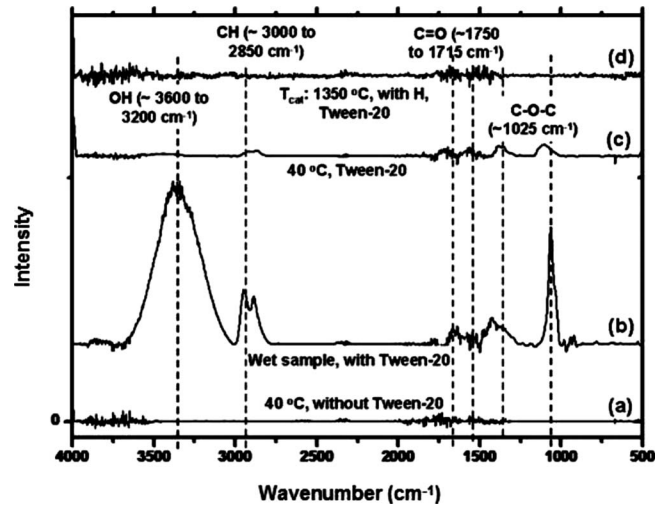
bond at 1750–1715 cm^{-1}, and C—O—C bond in ring (sometimes called tetrahydrofuran) at about 1025 cm^{-1} can be observed in IR spectra.

Figure 8 shows the difference of IR spectra of Ag functional liquid before and after annealing in H atoms. Without tween-20, spectrum (a) is very smooth. When tween-20 was added, specific peaks for tween-20 appear in spectrum. The peaks annealed with tween-20 are shown in spectrum (b) from wet sample. After drying at 40 °C, only hydroxide group in solution is removed, as shown in spectrum (c). After exposure to H atoms, spectrum (d) becomes similar to spectrum (a), which does not contain tween-20. From the figure, it can be confirmed that C-related bonds are removed from the metal films to realize low-resistivity in metal lines.

Figure 9 also shows the resistivity of metal lines as a function of the width of metal lines for the case of T_{cat} of 1350 °C and exposure time of 25 min. It is found that resistivity as low as 4×10^{-6} Ω cm can be realized for narrow metal lines of a width of 10 μm. The resistivity of bulk Ag itself is believed to be about 1×10^{-6} Ω cm. The minimum resistivity obtained in the present experiment is still larger
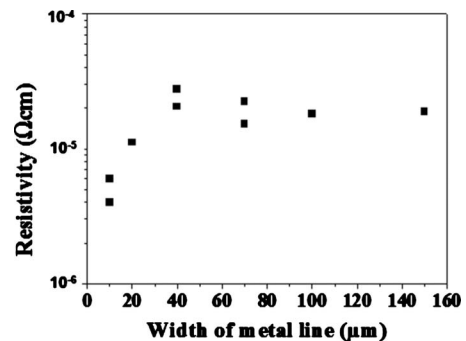

FIG. 7. Resistivity of metal lines as a function of annealing times for T_{cat} of 1350 °C and gas pressure of 100 Pa.

FIG. 9. Resistivity of metal lines as a function of width of lines.

JVST B - Microelectronics and Nanometer Structures

than that. However, our value appears almost equivalent to these obtained by vacuum evaporation or sputtering method. The resistivity was evaluated for both straight lines and the lines with two corners, as shown in Fig. 1. However, the measured resistivity for such two types of patters is not so different and within experimental errors from 4 to 6 $\times 10^{-6}$ Ω cm for 10 μm width lines.

IV. DISCUSSION

A. Capillary effect

When the contact angle of the liquid is large, the liquid is likely to make a sphere at the edge of the trench, and such a sphere cannot be broken due to its surface tension, and thus the liquid cannot get into the trench. As shown in Fig. 4, the original functional liquid has a contact angle of about 60° on the surface of the CPO substrate without a PTFE film, and does not appear hydrophilic enough to break the sphere made by the strong surface tension.

The tween-20 is a well-known surfactant to reduce the contact angle and also the surface tension.[12] The mechanism to reduce the contact angle has been studied in other literature.[13] From the results shown in Fig. 4, it can be speculated that the surfactant is always concentrated on the surface layer of the liquid sphere, and works to reduce the surface tension, because the contact angle is likely to saturate when VR exceeds just 5/1000. That is, after covering the surface layer of a liquid-sphere with the tween-20 molecules, the tween-20 does not appear to have any more effect on reducing the surface tension.

The contact angle of the liquid on the PTFE-coated CPO substrates is kept over 80°–90°. The contact angle larger than 90° is a measure of appearance of hydrophobic property. However, although the value is clearly below 90°, the migration of the liquid on the substrate surface still appears effective, at least, within the distance of about 4 mm, judging from the results shown in Fig. 5. As indicated in Fig. 1, the distance between two straight lines is kept 4 mm. This means that the liquid dropped at the middle of two lines should migrate to one of the trenches in such a distance to form metal lines. That is, the hydrophobicity is enough for the present purpose.

B. Electrical property and morphology

After treating metal lines by H atoms in the Cat-CVD chamber, the electrical properties of metal lines were remarkably improved. The annealing at temperatures around 40 °C as a drying process affects the property of metal lines by evaporating solvents from functional liquid. The resistivity of metal lines was reduced to the order of 10^{-2} Ω cm by this process. Such values of resistivity were often observed before H treatments.

The metal lines were shrunk enormously during the removal process of C-related compounds. Actually, the thickness of the metal line, estimated from SEM observation, was about 1.6 μm before treatment, while it was reduced to 1.0 μm after the treatment with H atoms generated at T_{cat} of
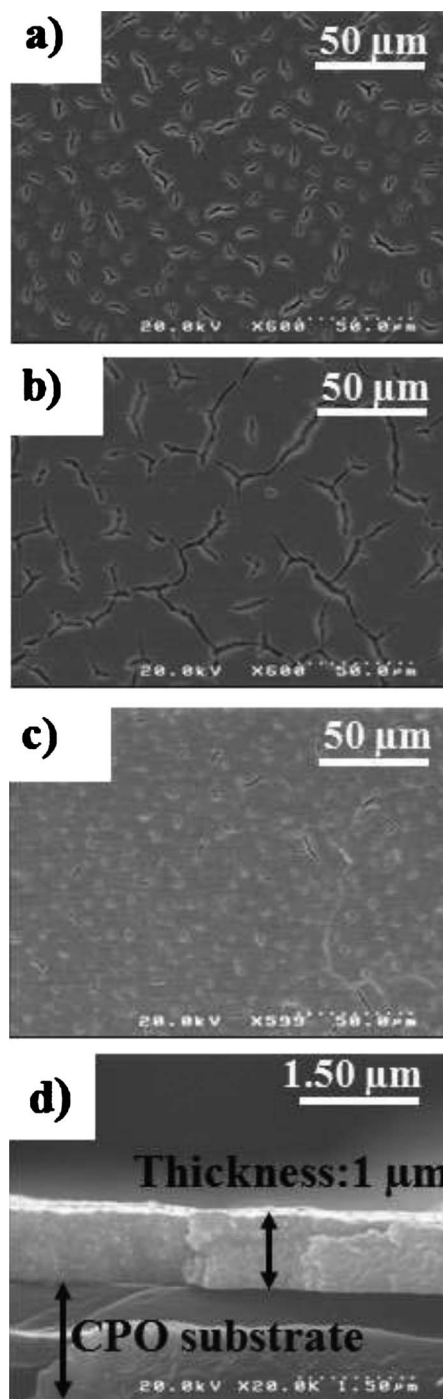

FIG. 10. Plane view of SEM images of metal surface after annealing by (a) drying process at 40 °C on a hot-plate, (b) the thermal radiation from the catalyzer at 1350 °C in vacuum, and (c) the thermal radiation from the catalyzer at 1350 °C with exposure to H atoms. (d) The cross-sectional SEM image of the metal layer shown in (c).

1350 °C. The thickness of metal lines was 0.7–1 μm for the metal lines with widths from 10 to 150 μm. The structure after the shrinking process appears dependent on the method to remove C atoms from the metal lines. Figures 10(a)–10(c) show the SEM plane views of metal lines after annealing steps. Figure 10(a) shows the view just after 40 °C drying process, indicating the existence of many cracks. Figure

10(b) shows the view after heat-treatment by utilizing the thermal radiation from the catalyzing wire of T_{cat} of 1350 °C inside the Cat-CVD chamber, but H_2 gas was not introduced. It is estimated that the CPO substrate is heated to temperatures over 100–150 °C by the thermal radiation, since the system used in the present experiment does not have a proper cooling system in the substrate holder. The figure demonstrates that the cracks are growing, probably because C-related compounds in the metal lines accumulate at certain regions, and then large gas-bubbles are formed at near cracks during heating.

On the other hand, when H_2 gas was introduced, the organic compounds were fragmented into volatile hydrocarbon molecules by the reaction with H atoms,[14] and such small fragments escaped from the metal lines smoothly. Metal nanoparticles may migrate and be reconstructed to form dense metal films after C-related compounds are removed. Thus, the cracks did not grow so much, but during this process, grains consisting of many metal nanoparticles grew to larger size. Figures 10(c) and 10(d) show the plane view after H atom treatment and the cross-sectional view of the metal line with a thickness of 1 μm, respectively. The structure appears denser than the case shown in Fig. 10(a). The resistivity appears strongly dependent on the morphological structure after treatment.[15] The dense structure may be suitable to obtain low resistivity.

The growth of cracks may also be the reason why the resistivity depends on the width of metal lines. When the width is large, the shrinkage after heat-treatment may be large and the possibility of cracks with large spaces may increase, even if H treatment is applied. Figures 11(a) and 11(b) show the photographs of SEM plane views for 10- and 150-μm-wide lines, respectively. Although the reason why the resistivity is likely to decrease at the width of 10 μm, as shown in Fig. 9, is not exactly explained quantitatively, this figure clearly shows that serious cracks are observed for lines with larger width. This might be the reason why the resistivity depends on the line width.

This is a non-negligible drawback of the technique at the moment and it must be solved for further development. Probably, the dropping of functional liquid twice on cracked lines might be a solution. In addition to it, the optimization of T_{cat} and/or substrate temperature during H treatment or the tuning of the concentration of Ag functional liquid might be another solution.

One may worry about the dependence of resistivity on the patterns. The resistivity was evaluated from both straight lines and lines with two corners as already mentioned. The difference of resistivity for different patterns was not clearly observed for 10 μm width lines. This is also hold for even 150 μm width lines, although the magnitude of shrinkages is apparently different between 10 μm width lines and 150 μm ones. This is probably due to the fact that the density of cracks induced by shrinkage may not depend on the patterns so much.
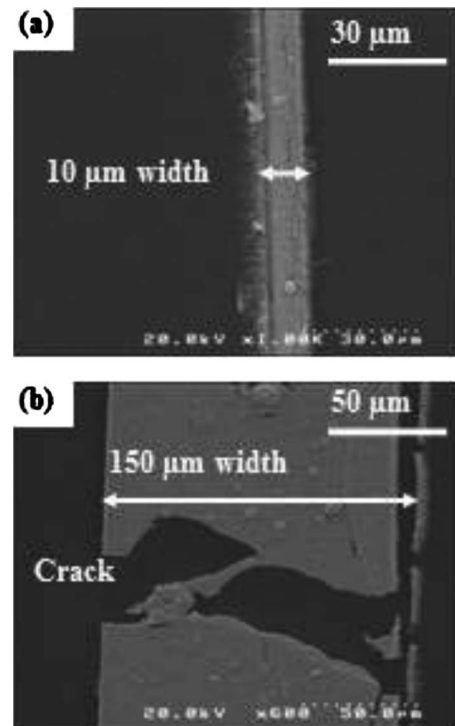

FIG. 11. SEM images of the surface of metal lines with widths of (a) 10 μm and (b) 150 μm, after exposure for 25 min to H atoms generated at T_{cat} of 1350 °C.

V. CONCLUSION

A novel technique for fabricating metal lines using metallic functional liquid has been proposed and its feasibility has been demonstrated. Ag lines are formed by successive dropping and drying Ag functional liquid on the PTFE-covered CPO plastic substrate in a quick, automatic, and inexpensive manner. In this process, the hydrophobic PTFE film contributes to the precise formation of Ag lines, and tween-20 surfactant plays a dominant role for automatic formation of Ag line. In particular, the resistivity of Ag line was reduced to 4×10^{-6} Ω cm by exposing to H atoms generated by Cat-CVD apparatus. Thus, the formed Ag lines are able to satisfy the properties required for metal lines used in electronic devices, compared to conventional metal films.

Cracking in the wide line is still the non-negligible drawback of this current issue although the double dropping of liquid or other technique could solve problem in future. The results of this study are significantly meaningful for electronic device industry, especially for the low-cost fabrication of ultra large-scale displays.

[1]H. Matsumura, M. Ishikawa, K. Kida, K. Maenaka, T. Kuno, K.-h. Nitta, M. Terano, and S. Minami, Jpn. J. Appl. Phys., Part 1 **45**, 4413 (2006).
[2]A. Chang, Proceedings of the Seventh International Display Workshop (IDW00), Kobe, November 2000 (unpublished), p. 195.
[3]M. H. Frey, T. J. Berniard, and R. A. Boehmer, U.S. Patent, USPTO Application No. 20,080,150,148 (June 26, 2008).
[4]F. Laermer and A. Schlip, U.S. Patent No. DE4,241,045 (US-55,018,93) (June 23, 1994).
[5]J. Y. Kim, D. Sohn, and E.-R. Kim, Appl. Phys. (Berlin) **72**, 699 (2001).
[6]J. Y. Kim, E. R. Kim, Y. K. Han, K. H. Nam, and D. W. Ihm, Jpn. J. Appl. Phys., Part 1 **41**, 237 (2002).
[7]M. Takachi, H. Yasuoka, K. Ohdaira, T. Shimoda, and H. Matsumura, Thin Solid Films **517**, 3622 (2009).
[8]L. S. Livshits, L. P. Bakhrakh, I. D. Grebeshkova, and V. P. Teodorovich, Metal Sci. Heat Treat. **1**, 53 (1959).
[9]H. Umemoto, K. Ohara, D. Morita, Y. Nozaki, A. Masuda, and H. Matsumura, J. Appl. Phys. **91**, 1650 (2002).
[10]A. Izumi and H. Matsumura, Jpn. J. Appl. Phys., Part 1 **41**, 4639 (2002).
[11]K. Hashimoto, A. Masuda, H. Matsumura, T. Ishibashi, and K. Takao, Thin Solid Films **501**, 326 (2006).
[12]M. Singh, J. R. Orsenigo, and D. O. Shah, J. Am. Oil Chem. Soc. **61**, 596 (1984).
[13]X. Cui, S. Mao, M. Liu, H. Yuan, and Y. Du, Langmuir **24**, 10771 (2008).
[14]W. Tsang and J. A. Walker, J. Phys. Chem. **99**, 3156 (1995).
[15]H. Jiang, K.-S. Moon, J. Lu, and C. P. Wong, J. Electron. Mater. **34**, 1432 (2005).