Title	Low Resistivity Metal Lines Formed by Functional Liquids and Successive Treatment of Catalytically Generated Hydrogen Atoms in Cat-CVD System
Author(s)	Kieu, Nguyen Thi Thanh; Ohdaira, Keisuke; Shimoda, Tatsuya; Matsumura, Hideki
Citation	Thin Solid Films, 519(14): 4565-4567
Issue Date	2011
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/9834
Rights	NOTICE: This is the author's version of a work accepted for publication by Elsevier. Nguyen Thi Thanh Kieu, Keisuke Ohdaira, Tatsuya Shimoda, and Hideki Matsumura, Thin Solid Films , 519(14), 2011, 4565-4567, http://dx.doi.org/10.1016/j.tsf.2011.01.303
Description	

Low Resistivity Metal Lines Formed by Functional Liquids and Successive Treatment of Catalytically Generated Hydrogen Atoms in Cat-CVD System

Nguyen Thi Thanh Kieu[1,2], Keisuke Ohdaira[1], Tatsuya Shimoda[1], and Hideki Matsumura[1*]

[1]School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Nomi, Ishikawa, 923-1292, Japan, E-mail address: kieu-ntt@jaist.ac.jp, Tel: +81-761-51-1149, Fax: +81-761-51-1149

[2]Ho Chi Minh City Institute of Physics, No. 1, Mac Dinh Chi, District 1, Ho Chi Minh city, Vietnam

[*]Corresponding author: h-matsu@jaist.ac.jp

Abstract

Metal-interconnection among electrodes is an important process to fabricate electronic devices. A novel high-speed technique using silver (Ag) functional liquid to form Ag lines is proposed. For improvement of electrical conductivity of the Ag lines, atomic hydrogen (H) generated by Cat-CVD system is used. There is a sintering phenomenon among Ag nanoparticles (~50 nm) during H treatment at low substrate temperatures (~100^{o}C). Scanning electron microscopy (SEM) reveals that the Ag grain size increases with H annealing duration, which results in the resistivity of the Ag lines on the order of 10^{-6} Ω cm.

Keywords

Hydrogen treatment, Functional liquid, Metal line, Sintering

1. Introduction

Metal-interconnection among electrodes of transistors is conventionally formed by the deposition of metal films and successive photo-lithographic patterning process [1]. Recently, the printing technology using a metal-ink is developed. By this way, metal lines can be formed directly on a substrate without using expensive vacuum systems and photolithographic process, and also the configuration of metal lines can be easily designed and controlled in specific patterns [2].

Metal-interconnection is used in other types of devices. For instance, if a millions of integrated circuits (IC) chips are deposited at pixel positions and if many electrodes of such IC chips are connected with metal lines, fabrication of ultra large-scale flat panel displays over 2 m wide can be in target [3]. That is, the formation of metal lines and other functions from a droplet of specially designed liquids is important for future progress of new electronic devices.

We have studied to form metal lines on a plastic substrate by using functional liquid in which many nm-size metal particles are solved in organic solvent [4]. In particular, silver (Ag) nanoparticles are used due to their specific potential such as electrical conductivity, chemical durability, and optical properties [5]. Originally, the organic compounds in liquid are the drawback on the electrical conductivity of metal lines. As a novel solution, hydrogen (H) atoms generated catalytically from hydrogen molecules

(H_2) in Cat-CVD system is used to improve the electrical properties of metal lines [6]. The resistivity can be lowered to the order of 10^{-6} Ω cm, which is equivalent to that of the metal line formed by vacuum evaporation. Reducing the resistivity of Ag lines after H annealing is definitely related to the structure and morphology of Ag lines. Thus, the behaviors of Ag lines are studied in this paper.

2. Experimental Procedure

For forming metal lines on a plastic substrate, a mold of crystalline silicon (Si) wafer was made by Bosch etching process (Sumitomo MUC21 RD). This mold was imprinted onto a 200 μm-thick cyclic polyolefin "CPO" substrate, named "Zeonor" produced by Nippon Zeon Corporation, to form trenches which are used for the formation of metal lines. Before the imprint process started, the substrate was covered with a hydrophobic polytetrafluoroethylene (PTFE) thin film which was deposited by Cat-CVD with hexafluoropropyleneoxide (HFPO) as a source gas. During imprinting process, the PTFE at the positions of trenches is destroyed, and partially lost the hydrophobic properties. The functional liquid contains Ag nanoparticles, 1,3-propanediol, and pure water [4]. This liquid was added with a tiny volume ratio of Tween-20 surfactant (5/1000) for reducing contact angle on a CPO substrate. This work aims to gain the capillary effect of functional liquid inside trenches and form Ag lines automatically. These Ag lines on a CPO substrate were pre-heated at 40 ^{o}C for drying before exposed to H atoms. The surface image of a sample before H treatment is shown in Fig.1. During H treatment, the temperature of tungsten (W) catalyzer (T_{cat}) was set at 1350^{o}C and the processing time was fixed at 25 min. Gas pressure during H treatment was about 70-100 Pa, and a substrate temperature was ~100°C.

The electrical resistivity of the Ag lines was measured by the semiconductor parameter analyzer, HP 4156. The micro-structural morphology of the Ag line was observed by a scanning electron microscope (SEM), Hitachi S-4100. The functional liquid was dropped also on floating-zone (FZ) grown crystalline Si substrates with a resistivity of more than 1000 Ω cm, and then treated similarly to the Ag line forming process for analyzing the component and band-configuration of metal lines by using X-ray photoelectron spectroscopy (XPS, ESCA-5600) with a monochromatized Al K_α source (1486.6 eV) operated at 13.9 kV, and Fourier transform infrared (FT-IR, Shimadzu-8300) spectroscopy, in a transmission mode, respectively. Due to organic compounds in Ag liquid, the specific peaks for oxygen-hydrogen (O-H), carbon-hydrogen (C-H), carbon-oxygen (C=O), and carbon-oxygen-carbon (C-O-C) bonds can be observed in IR spectra.

3. Results and Discussions

Fig. 2 shows the difference of IR spectra for Ag functional liquid before and after drying and annealing in H atoms. After drying at 40^{o}C (see Fig. 2b), only hydroxide group in solution is removed, and thus, the metal line weight is largely reduced, near 90 %. (c) and (d) in Fig. 2 show that the peaks originating from organic compounds are still observed after 5 and 10 min annealing in H atoms. However, after exposure to H atoms in sufficient duration, 25 min (shown in Fig. 2e), the specific peaks of organic compounds definitely disappear although the percentage of weight loss is negligible. These results show that C-related bonds are removed from the metal films, by the effect of H atoms [7], to realize low-resistivity in metal lines.

Fig. 3 shows SEM plan views of Ag lines before and after H annealing at T_{cat} of 1350°C. It is revealed that there is no effect of H to Ag nanoparticle size if H annealing time is insufficient, as shown in Fig. 3b. However, after sufficiently long H annealing, C atoms were probably converted to volatile hydrocarbon molecules and they might escape from the Ag lines in small size individually. During H treatment for 10 and 25 min, the necks among Ag nanoparticles are formed as shown in Figs. 3c and 3d, respectively. This indicates that there are some reactions between H atoms and organic compounds, and the specific effect supports for sintering process among Ag nanoparticles at a low temperatures (~100°C) [8]. Moreover, to clarify the effect of H atoms, a Ag layer is also attempted to expose to Ar gas for 25 min. The resistivity of a Ag films was as high as ~10^{-2} Ω cm after exposure to Ar, and no noticeable variations can be seen in FT-IR spectrum and SEM image, as shown in (f) of Fig.2 and Fig. 3e. These results indicate that Ar gas cannot affect Ag lines, and the structure of the Ag nanoparticles is almost similar to that dried at 40°C. Thus, H atoms certainly have the unique properties which can significantly modify the microstructure of Ag lines**.**

Fig. 4 shows XPS spectra of Ag lines after drying at 40 °C and after 25-min H treatment. The signal of C atoms prevails in the spectrum of Ag lines after drying at 40 °C. The calculated atomic quantity summarized in Table 1 shows that Ag lines still contain a large amount of C atoms. Hence, the resistivity of Ag lines is as high as 10^{-2} Ω cm. However, after exposure to H atoms, C atoms mostly disappear, and Ag atoms dominate in Ag lines. One can see a clear O peak even in the spectrum of H-treated Ag lines. This is probably due to the humidity and O atoms just adsorb on the Ag line surface, meaning that the O atoms do not affect the electrical conductivity of Ag lines.

Indeed, the resistivity of Ag line is reduced to the order of 10^{-6} Ω cm. Because of the porous structure show in Fig. 3, the resistivity of the Ag lines appears slightly higher that made by other conventional methods. However, the value on the order of 10^{-6} Ω cm is still low enough for practical use of such Ag lines. Another advantage of this method is that the Ag lines are durable for bending the substrate.

4. Conclusions

The present study describes clearly that the Ag lines are definitely formed on a CPO plastic substrate by Ag functional liquid. Organic compounds are removed from Ag lines, and the neck growth among Ag nanoparticles occurs during H annealing. Thus, at low temperature (~100 ^{o}C), H atoms strongly affect to improve the electrical property because of the sintering phenomenon among Ag nanoparticles. The resistivity of Ag lines is remarkably reduced to the order of 10^{-6} Ω cm.

Acknowledgements

The authors thank Nippon Zeon Corporation for providing Zeonor films, and also thank Shimoda laboratory of JAIST for supplying original Ag ink. We are also grateful to K. Koyama, T. Hayakawa, and But-yeu, all from JAIST, for valuable discussion.

References

1. C.Y. Chang, S.M. Sze, ULSI Technology, McGraw-Hill Companies, 1996, p. 379.

2. M.H. Frey, T.J. Berniard, R.A. Boehmer, U.S. Patent, USPTO Application No.#20080150148, 26 Jun. 2008.

3. H. Matsumura, M. Ishikawa, K. Kida, K. Maenaka, T. Kuno, K. Nitta, M. Terano, S. Minami, Jpn. J.Appl. Phys. 45 (2006) 4413.

4. N.T.T. Kieu, K. Ohdaira, T. Shimoda, H. Matsumura, J. Vac. Sci. Technol. B 28, (2010) 775.

5. L.T. Chang, C.C. Yen, J. Appl. Polym. Sci. 55 (1995) 371.

6. Y. Kumashiro, H. Nakako, M. Inada, K. Yamamoto, A. Izumi, M. Ishihara, Appl. Surf. Sci. 256 (2009) 1019.

7. X. Cui, S. Mao, M. Liu, H. Yuan, Y. Du, J. Langmuir 24 (2008) 10771.

8. S.L. Hsu, R. Wu, J. Materials letters 61 (2007) 3719.

List of tables and figure captions

Table 1 Atomic percentage (%) in Ag lines calculated using XPS data

Fig.1 Ag lines on a CPO substrate with various widths from 10 to 150 μm after drying at 40^{o}C.

Fig.2 FT-IR spectra of a Ag functional liquid (a) before drying; (b) after drying at 40 ^{o}C; (c)-(e) after drying at 40 ^{o}C and exposure to H atoms for 5, 10, and 25 min, respectively; (f) after drying at 40 ^{o}C and exposure to Ar gas for 25 min.

Fig.3 The plan-view SEM images of Ag surfaces after (a) drying at 40 ^{o}C on a hot-plate; (b)-(d) drying and exposure to H atoms for 5, 10, and 25 min, respectively; (e) drying and exposure to Ar for 25 min.

Fig.4 XPS spectra of Ag surfaces after annealing by (a) drying process at 40 ^{o}C on a hot-plate; (b) the thermal radiation from the catalyzer at 1350 ^{o}C with exposure to H atoms for 25 min.

Table 1

	Drying at 40 ^{o}C	H treatment
Ag 3d	8.05	56.72
O 1s	23.31	43.28
C 1s	70.64	0

Figure 1

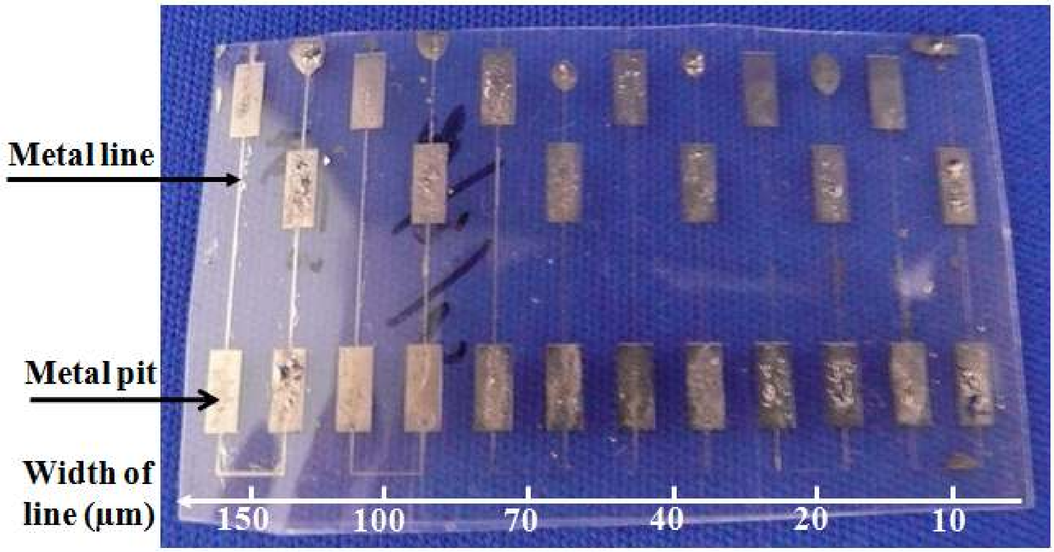
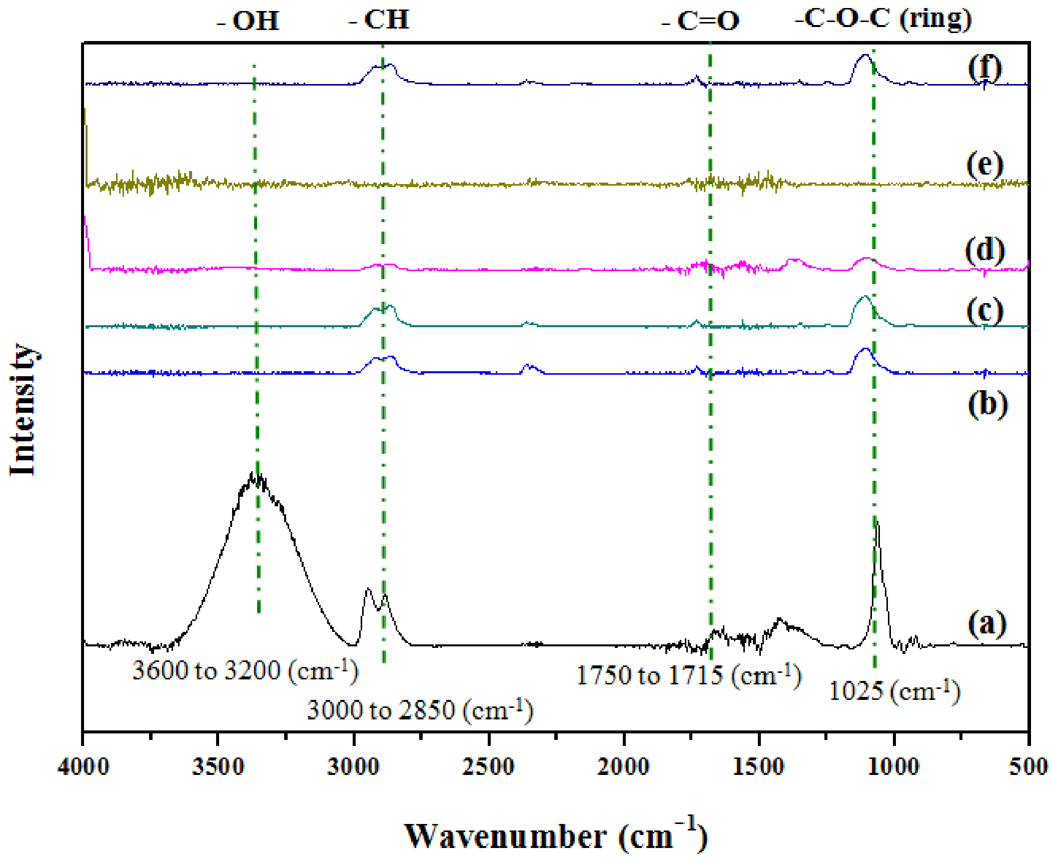
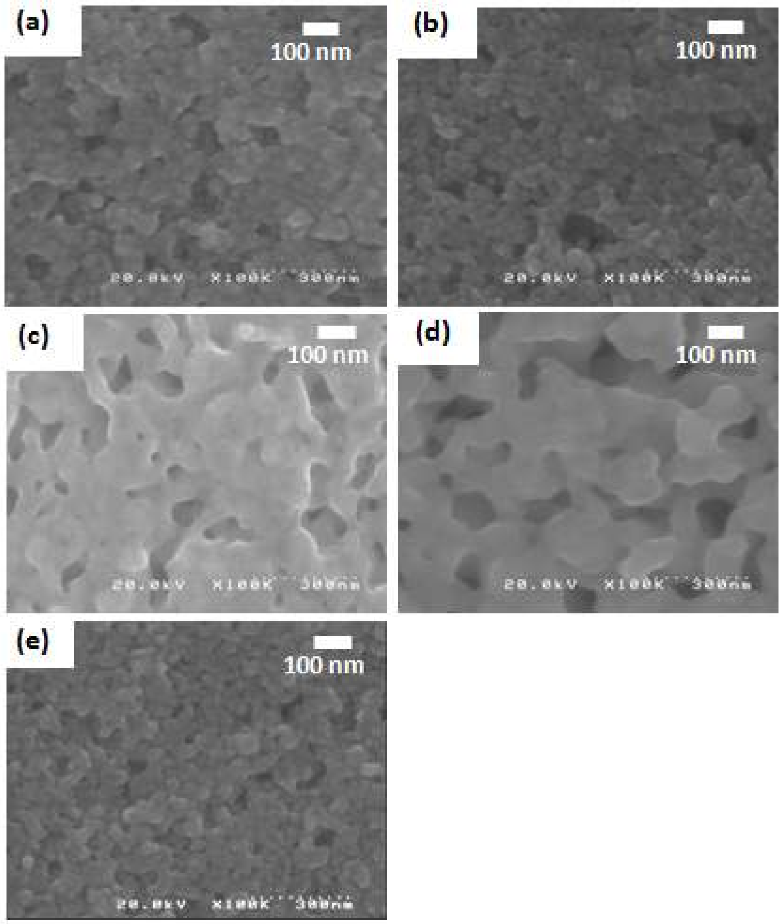


Figure 2



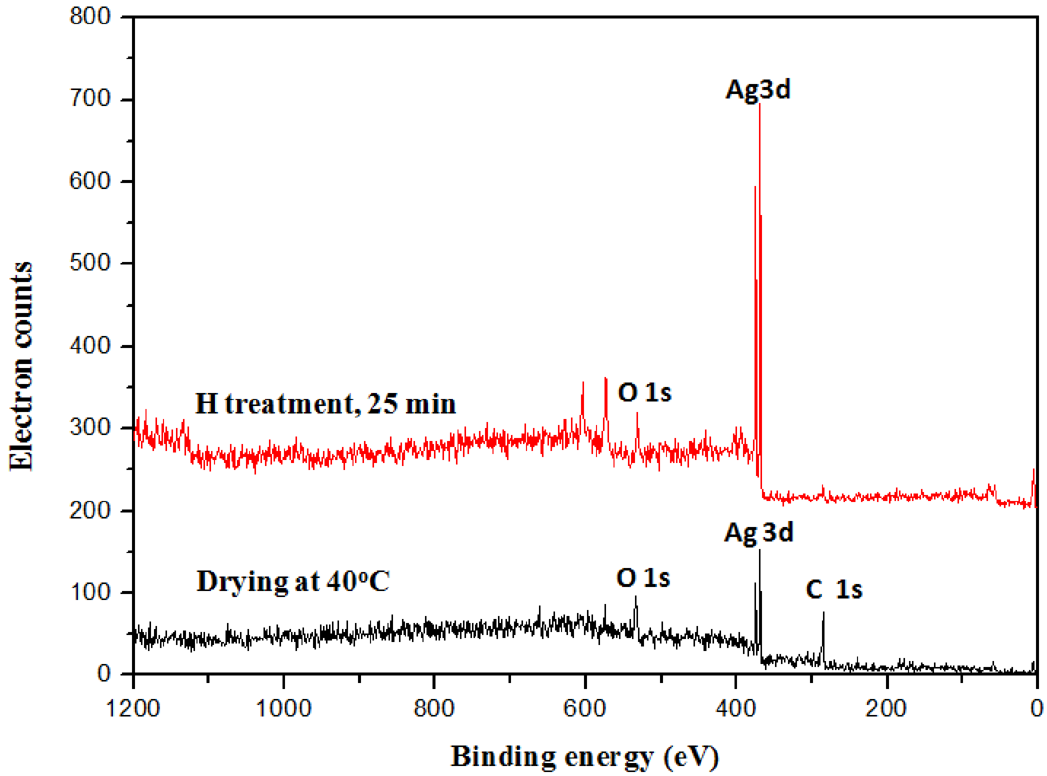
- OH
- CH
- C=O
-C-O-C (ring)
(f)
(e)
(d)
(c)
(b)
(a)
Intensity
3600 to 3200 (cm-1)
3000 to 2850 (cm-1)
1750 to 1715 (cm-1)
1025 (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

Figure 3



(a)
100 nm
20.0kV X100K 300nm
(b)
100 nm
20.0kV X100K 300nm
(c)
100 nm
20.0kV X100K 300nm
(d)
100 nm
20.0kV X100K 300nm
(e)
100 nm
20.0kV X100K 300nm

Figure 4


Ag3d
O 1s
H treatment, 25 min
Ag 3d
Drying at 40°C
O 1s
C 1s
Electron counts
Binding energy (eV)
800
700
600
500
400
300
200
100
0
1200
1000
800
600
400
200
0