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Study on Surface Characteristic of the Copper Nitride Films by Absorbed Oxygen

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SUMMARY The copper nitride surface characteristics according to atmospheric pressure plasma (APP) and excimer ultraviolet (EUV) treatment were compared using XPS and AFM. As the result of XPS analysis result, in C1s, the organic material removal effect was greater for EUV treatment than for APP, and the oxygen content was found to be low. In Cu (933 eV) area, the shoulder peak of Cu compound was detected, and the reduction was greater for EUV processing than for APP. In the AFM phase image which could be analyzed using the superficial viscoelasticity, the same trend was observed. On the copper nitride surface, the weak boundary O layer is formed according to the clean processing, and such phenomenon was interpreted as a factor for lowering the affinity with polymer.

key words: *copper nitride, weak boundary layer, oxygen, atmospheric pressure plasma, excimer ultraviolet, XPS, AFM*

1. Introduction

Copper has high conductivity and is an important material in micro-pattern forming and low-reflection efficiency. However, it becomes oxidized in the air to form Cu_2O natural oxide film [1], thus copper nitride (CuNx) is hard to keep the surface state. There are reports on the surface characteristics of CuNx film itself through temperature stability [2], [3], radio-frequency magnetron sputtering [4]–[6] and electro characteristic using laser [7]. To understand the mutual relationship between copper and polymer, it is necessary to study the oxygen behavior on the CuNx surface according to surface processing.

A surface treatment technology of removing organic pollutants to secure affinity between layers of material and printing ability is demanded in a display industry for miniaturization and densification. Organic pollutants affect inequality and yield of product quality, and hydrophilicity to clean organic pollutants on the surface can increase wet cleanse effect. APP and EUV are one of the material surface treatment devices, have the merit of improving surface reforming characteristics such as adhesiveness and stickiness by drying the surface in a short period of time. APP treatment technology is attracting attention as it reduces production cost by enabling plasma processing under air pressure and improving the speed of processing [1], [8]–[10].

APP has a simple device and is applied to LCD manufacturing process as a pretreatment idea because of its simple use. And it is a method of removing organic matters by oxidizing by O radical and O ion through plasma discharge. In general, it is widely applied to all processes of cleaning organic matters and forming a thin film, and it is also applied to wet etching. Remaining PR after development of photo resist pattern causes stain but it can be improved by improving removal of organic matters and wetting property through APP treatment. EUV removes organic matters and creates hydrophilicity by reacting with organic matters through oxidizing the substrate surface by creating ozone with a method of cutting organic matter combination with energy wavelength (172 nm) emitted from the lamp using features of Excimer lamp [11]–[13]. It is generally used in pretreatment of Dry and all cleansing of evaporation process with low pressure mercury lamp in LCD manufacturing process [14], [15].

Both have same characteristic of improving printing property by removing unnecessary organic matters through creation of oxygen (O) radical. However, there is a case where removal of organic matters on the substrate surface is accomplished effectively and there is a case where adhesiveness and stickiness strength as hydrophilicity decreases according to substrate materials that are being processed [16]. Effectiveness according to treatment of substrate is partially interpreted with weak boundary layer created on the surface [17], [18], but precise chemical characteristic analysis about effect of low molecular weight substances of surface is required.

This study is about chemical characteristics of each surface of CuNx substrate according to use of EUV and APP, and it compared using XPS and AFM analysis. A surface cleansing technology can be applied to various fields such as surface reforming, cleansing, adhesive property, and stickiness property improvement. Basic study on substrate surface is needed to secure stable quality of a production line.

2. Experimental

In order to compare the influence according to surface treatment conditions, the APP and EUV treatment were applied to the CuNx substrate once/twice each. CuNx substrate is made in vacuum chamber with Cu target which is Ar 500 sccm, N_2 2500 sccm provided and 40 kW, 15 seconds deposited. The CuNx thickness was 40~50 nm.

The cleansing conditions is 70~75 kW, N_2 8000~9000

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lpm, CDA 50~55 lpm for the APP, and 200 mJ UV energy (UV Power: 50 mW/cm^2, Irradiation time: 4 sec) using 172 nm spectrum for the EUV. Clean-treated substrate was compared through XPS and AFM analysis. XPS equipment use Thermo Corporation that X-ray source is aluminum Ka 1487 eV. NanoScope IV AFM of digital instruments was used in the tapping mode. Things that play the biggest role for decomposing organic substances in APP and EUV treatment are oxygen radical (O*) and ozone (O_3) created by processing oxygen with plasma and there is hydroxyl (-OH) that is created by decomposing of vapor of air.

3. Results and Discussion

Figure 1 shows XPS analysis result about the surface before and after EUV and APP treatment on CuNx substrate. Figure 1(b) shows C1s area with the spectrum results. As the result of (b) C1s, it was confirmed that C-C and C-H peak are shown low if the surface is treated with APP and EUV. Organic pollutants on CuNx surface are all removed from both. However, there was a tendency of increasing oxygen (O) products in C-O and O-C=O peak area. In particular, the yield of oxygen (O) after APP treatment than EUV had increased. Figure 1(c) showed result of spectrum at Cu (932.4 eV) area. It was confirmed to have a significant reduction in cleansing effect according to surface treatment compared to reference sample (ⓐ). The location of each spectrum shows CuO (933.6 eV), $Cu(OH)_2$ (934.8 eV), $CuCO_3$ (935 eV), and the removal effect according to EUV treatment against APP appeared great.

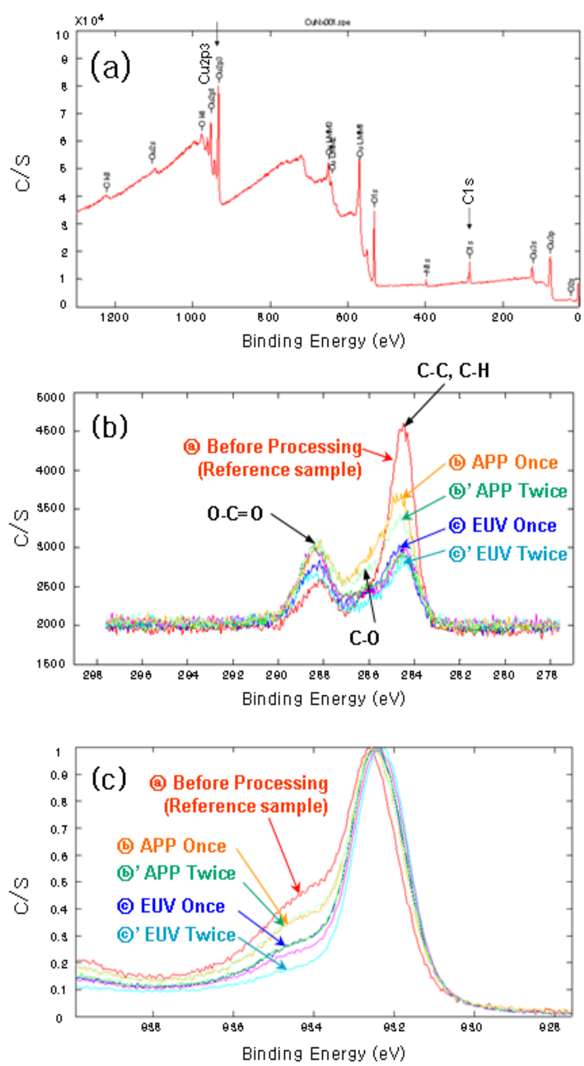

Fig. 1 (a) XPS analysis result of copper nitride flim (b) C1s and (c) Cu (932.4 eV) area analysis result of CuNx before and after APP and EUV treatments.

As explained earlier, for the case of APP treatment, if AC electric field is applied to counter electrodes then electron within the gas reacted with electric field is accelerated as high energy and creates oxygen ion (O^{2+}) by crashing with oxygen molecule or it is separated into oxygen atom ion ($2O^+$). As ion condition is very unstable, it becomes oxygen radical (O*) by combining with surrounding electrons or creates ozone (O_3) by combining with other oxygen ions, and ozone is once again decomposed into oxygen molecule and oxygen radical by crashing with electron. Hydrocarbons are often connected in a loop form for organic matters, and radicals created from APP device disconnect these loops and removes organic matters through decomposition. On the other hand, for EUV treatment, removal of organic matters is same as APP but it was confirmed through XPS result that oxygen layers remaining on CuNx surface due to oxidation by ozone through discharge of the excimer are created less than APP. As a result of processing polymer printing on CuNx that is treated with EUV and APP, polymer printing effectiveness is noticeably inferior in the condition that is treated with APP. A contact angle was also created less in the condition that is treated with EUV. In general, organic substrate such as a polymer shows equal tendency of printing effectiveness by declining of a contact angle. Both have an effect on printing property between other polymer materials by newly creating hydrophile chemical combinations such as -COOH and C=O. APP has an effect of increasing contact area by creating fine unevenness on the surface. CuNx, however, showed different result than the generally understood results. Then what is the reason that adhesion occurs on the substrate surface according to cleansing process?

The cause of occurrences was shown in Fig. 2. In general, copper creates an oxide film by contacting with oxygen in the air and a contact angle increase [19]. Natural oxide created on the copper surface is Cu_2O and it is reported to be creating weak boundary layer due to of lattice constant [17]. As shown in Fig. 2(a), a weak boundary O layer is created as main on the copper surface for the cased of APP because it is cleansed by oxygen radical and oxygen ion. Consequentially, an oxygen layer is adsorbed on CuNx surface which is the main factor of reducing contact angle with other polymer organic materials. It could predict that same status occurs in Mg^{2+} and Cr^{2+} which create a same metallic oxide. On the other, when EUV treatment is done as in Fig. 2(b), matching

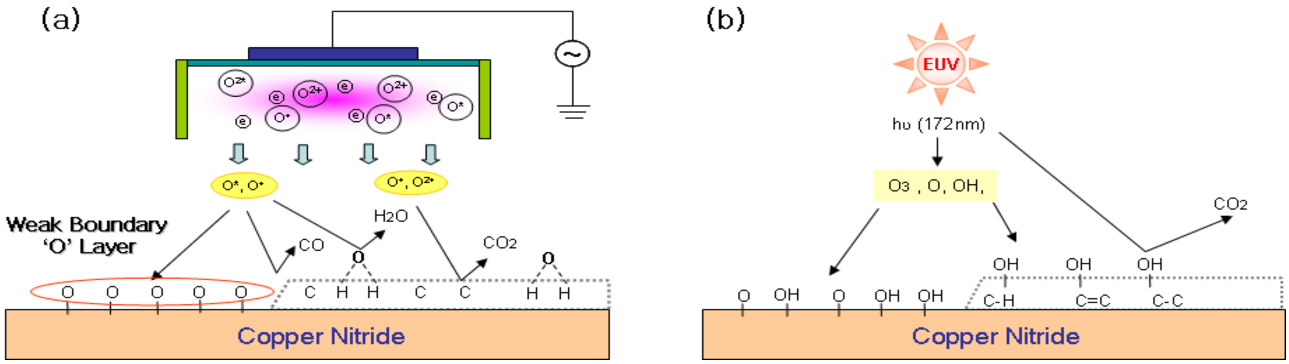

Fig. 2 The mechanism of the oxygen absorption on copper nitride surface by (a) APP and (b) EUV treatment conditions. Oxygen radical and oxygen ion through plasma discharge create a weak boundary layer on copper nitride surface.

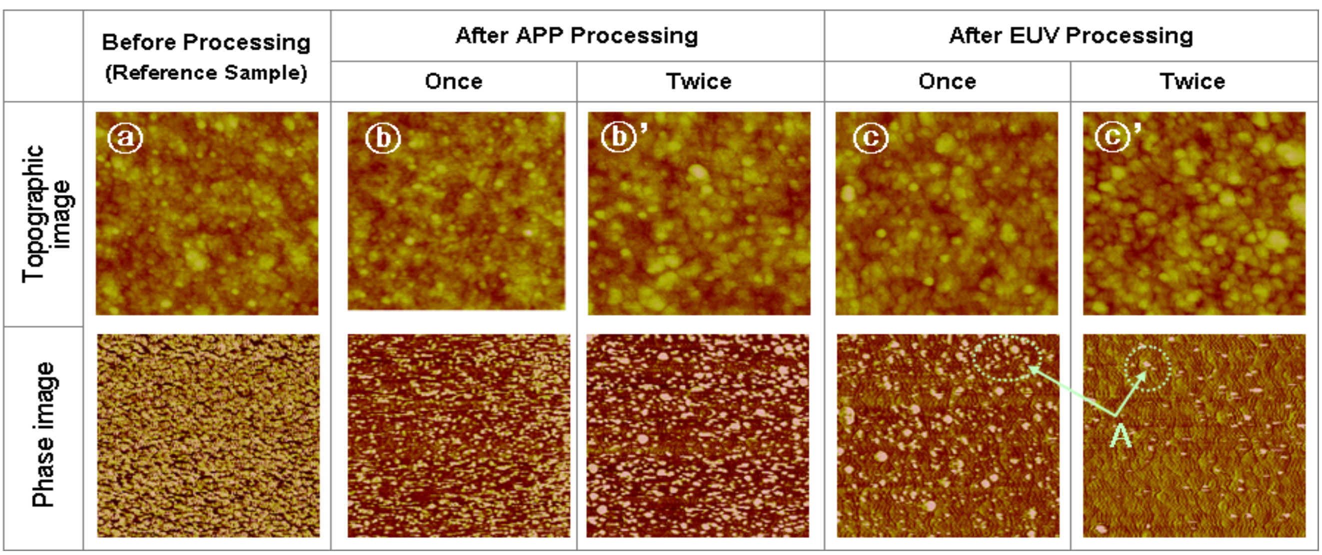

Fig. 3 AFM images (Scan size 800 nm sq.) of copper nitride result before and after APP and EUV treatments.

with organic matters is shown as good as oxygen remaining on CuNx surface partially exists. It was possible to confirm creation of an oxygen layer on CuNx surface according to cleansing condition through XPS analysis.

Figure 3 shows the AFM result at the CuNx surface according to each condition. First, there was no big different when looking at the topographic image through eyes. As a result of checking surface roughness, reference sample ⓐ before cleansing was 1.45 nm, APP treated ⓑ, ⓑ' were each 1.54 and 1.60 nm, and EUV treated ⓒ and ⓒ' were each 1.43 and 1.46 nm. Surface change almost did not show on the case of EUV treatment but fine shape of unevenness are created partially for the case of APP. As a result of analyzing AFM phase image that can compare each different component due to viscoelasticity [20]–[22], difference of shade on phase separation was shown clearly. For the case of ⓒ' that is treated with EUV 2 times, difference of shade on the surface is noticeably reduced and distributed as shown in A mark contrasting to ⓐ condition (Fig. 4). Phase image difference had shown 12° for reference sample (a) before cleansing, each 9.27° and 7.96° for the APP treated ⓑ and ⓑ', and each 5.92°, 4.25° for the EUV treated ⓒ and ⓒ'. This shows same tendency as XPS result that is shown according to removal of organic matters on CuNx surface with APP and EUV treatment. It is viewed as a condition

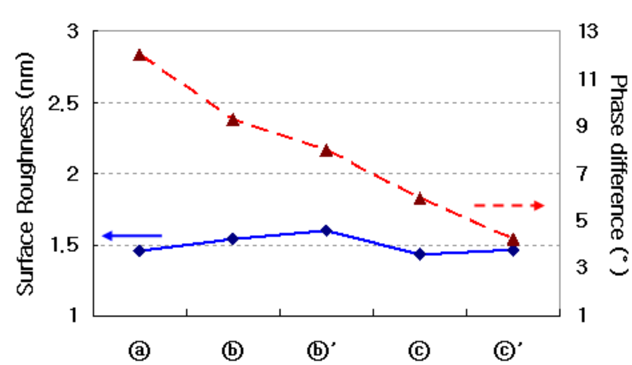

Fig. 4 The result of surface roughness and phase difference of copper nitride before and after APP and EUV treatments.

where organic components are removed due to reduction by C-C according to APP and EUV treatment. Sample ⓐ is formed same as the specimen that adsorbed water in atmosphere [23]–[25], AFM phase image shows EUV cleansing effect is greater than the APP. The surface and adsorption form could be compared by directly analyzing CuNx surface using AFM.

4. Conclusion

APP and EUV treatment were compared that used dry cleansing treatment in LCD process. The chemical characteristics on CuNx surface were different based on treatment conditions. Both are equal for removing organic matters, but oxygen component remaining on the surface was detected through XPS analysis for the case of APP treatment and it created a weak boundary O layer. Affinity of Cu material with oxygen is the main factor and it was confirmed that it is shown differently according to material characteristic of substrate. Various element materials are being developed to enhance LCD characteristics. To secure quality, the matching with other factories based on accurate analysis results for the surface status of the film itself is most important. Various analysis applications on film analysis using XPS and AFM are expected as an important measure of improving surface of all kinds of materials including electronic products and LCD.

References

[1] Y. Sawada, "Applications of atmospheric pressure glow plasma," J. Plasma Fusion Res., vol.79, no.10, pp.1022–1028, 2003.
[2] Y. Du, R. Huang, R. Song, L.B. Ma, C. Liu, C.R. Li, and Z.X. Cao, "Effect of oxygen inclusion on microstructure and thermal stability of copper nitride thin films," J. Mater. Res., vol.22, no.11, pp.3052–3057, 2007.
[3] Z.Q. Liu, W.J. Wang, T.M. Wang, S. Chao, and S.K. Zheng, "Thermal stability of copper nitride films prepared by rf magnetron sputtering," Thin Solid Films, vol.325, pp.55–59, 1998.
[4] T. Nosaka, M. Yoshitake, A. Okamoto, S. Ogawa, and Y. Nakayama, "Copper nitride thin films prepared by reactive radio-frequency magnetron sputtering," Thin Solid Films, vol.348, pp.8–13, 1999.
[5] S. Ghosh, F. Singh, D. Choudhary, D.K. Awasthi, V. Ganesan, P. Shah, and A. Gupta, "Effect of substrate temperature on the physical properties of copper nitride films by r.f. reactive sputtering," Surface and Coatings Technology, vol.142-144, pp.1034–1039, 2001.
[6] X.M. Yuan, P.X. Yan, and J.Z. Liu, "Preparation and characterization of copper nitride films at various nitrogen contents by reactive radio-frequency magnetron sputtering," Materials Letters, vol.60, pp.1809–1812, 2006.
[7] C. Gallardo-Vega and W. de la Cruz, "Study of the structure and electrical properties of the copper nitride thin films deposited by pulsed laser deposition," Appl. Surf. Sci., vol.250, pp.8001–8004, 2006.
[8] S. Kanazawa, M. Kogoma, T. Moriwaki, and S. Okazaki, "Stable glow plasma at atmospheric," J. Physics D., vol.21, pp.838–840, 1988.
[9] T. Yokoyama, M. Kogoma, T. Moriwaki, and S. Okazaki, "The mechanism of the stabilisation of glow plasma at atmospheric pressure," J. Phys. D: Appl. Phys., vol.23, pp.1125–1128, 1990.
[10] Y. Sawada, K. Yamazaki, N. Taguchi, and T. Shibata, "Pretreatmet of Ni/Au and Cu plating applied with atmospheric pressure plasma jet," J. Microelectronics and Packaging, vol.2, pp.189–196, 2005.
[11] B. Eliasson and U. Kogelschatz, "UV excimer radiation from dielectric-barrier discharges," Appl. Phys., vol.B46, pp.299–303, 1988.
[12] U. Kogelschatz, "Slient-discharge driven excimer UV sources and their applications," Appl. Surf. Sci., vol.54, pp.410–423, 1992.
[13] P. Bergonzo, P. Petal, I.W. Boyd, and U. Kogelschatz, "Development of a novel large area excimer lamp for direct photo deposition on thin films," Appl. Surf. Sci., vol.54, pp.424–429, 1992.
[14] D.L. Baulch, R.A. Cox, P.J. Crutzen, R.F. Hampson, J.A. Kerr, J. Troeand, and R.T. Watson, "Evaluated kinetic and photochemical data for atmospheric chemistry," J. Phys. Chem. Ref. Data, vol.11, no.2, pp.327–335, 1982.
[15] B. Eliasson and U. Kogelschatz, "Ozone generation with narrowband UV radiation," Ozone, vol.13, no.3, pp.365–373, 1991.
[16] Z. You and J. Dong, "Surface properties of treated ITO anodes for organic light-emitting devices," Appl. Surf. Sci., vol.249, no.1-4, pp.271–276, 2005.
[17] A.J. Kinlosh, Adhesion and adhesives, p.144, Chapman & Hall, 1987.
[18] J.M. Park and J.P. Bell, Adhesion Aspects of Polymeric Coatings, ed. K.L. Mittal, p.205, Plenum Press, New York, 1983.
[19] Y. Sawada, N. Taguchi, and K. Tachibana, "Reduction of copper oxide thin films with hydrogen plasma generated by a dielectric-barrier glow discharge," Jpn. J. Appl. Phys., vol.38, pp.6506–6511, 1999.
[20] A. Rasmont, Ph. Leclere, C. Doneux, G. Lambin, J.D. Tong, R. Jerome, J.L. Bredas, and R. Lazzaroni, "Microphase separation at the surface of block copolymers, as studied with atomic force microscopy," Colloids and Surfaces B, vol.19, pp.381–395, 2000.
[21] Q. Zhang, O.K. Tsui, B. Du, F. Zhang, T. Tang, and T. He, "Observation of intered phases in poly(styrene-b-butadiene-b-syrene) triblock copolmer by sovent-induced orde," Macromolecules, vol.33, pp.9561–9567, 2000.
[22] M.S. Kwak, H.R. Chung, J.-Y. Lee, J.H. Choi, K.R. Kim, S.P. Hong, C.H. Park, S.H. Choi, S.M. Lee, and C.G. Lee, "Characteristics of hybrid type alignment film in color TFT-LCD," IDW'07, LCTp7-8, 2007.
[23] K. Kuriyama, S. Shimizu, K. Eguchi, and T.P. Russell, "Development of poly(imide-*b*-amic acid) multiblock copolymer thin film," Macromolecules, vol.36, pp.4976–4982, 2003.
[24] K. Miura, "Water adsorption on a BaF2(111) surface in air observed with force microscopy," Phys. Rev., vol.B52, no.11, pp.7872–7875, 1995.
[25] A.L. Shluger, R.M. Wilison, and R.T. Williams, "Theoretical and experimental investigation of force imaging at the atomic scale on alkali halide crystals," Phys. Rev., vol.B49, no.7, pp.4915–4930, 1994.

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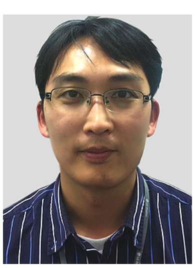

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