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2. **“The Development of Polyethylene Naphthalate Films by Low-pressure High-frequency Plasma Chemical Vapor Deposition System with Advance Oxidations Process”**, Journal of Advance oxidation technologies, Vol. 18, No. 1, January 2015, pp. 123-128.
3. **“Development of low-pressure high-frequency plasma chemical vapor deposition method on surface modification of silicon wafer”**, Vacuum, Vol. 109, July 2014, pp. 166-169.

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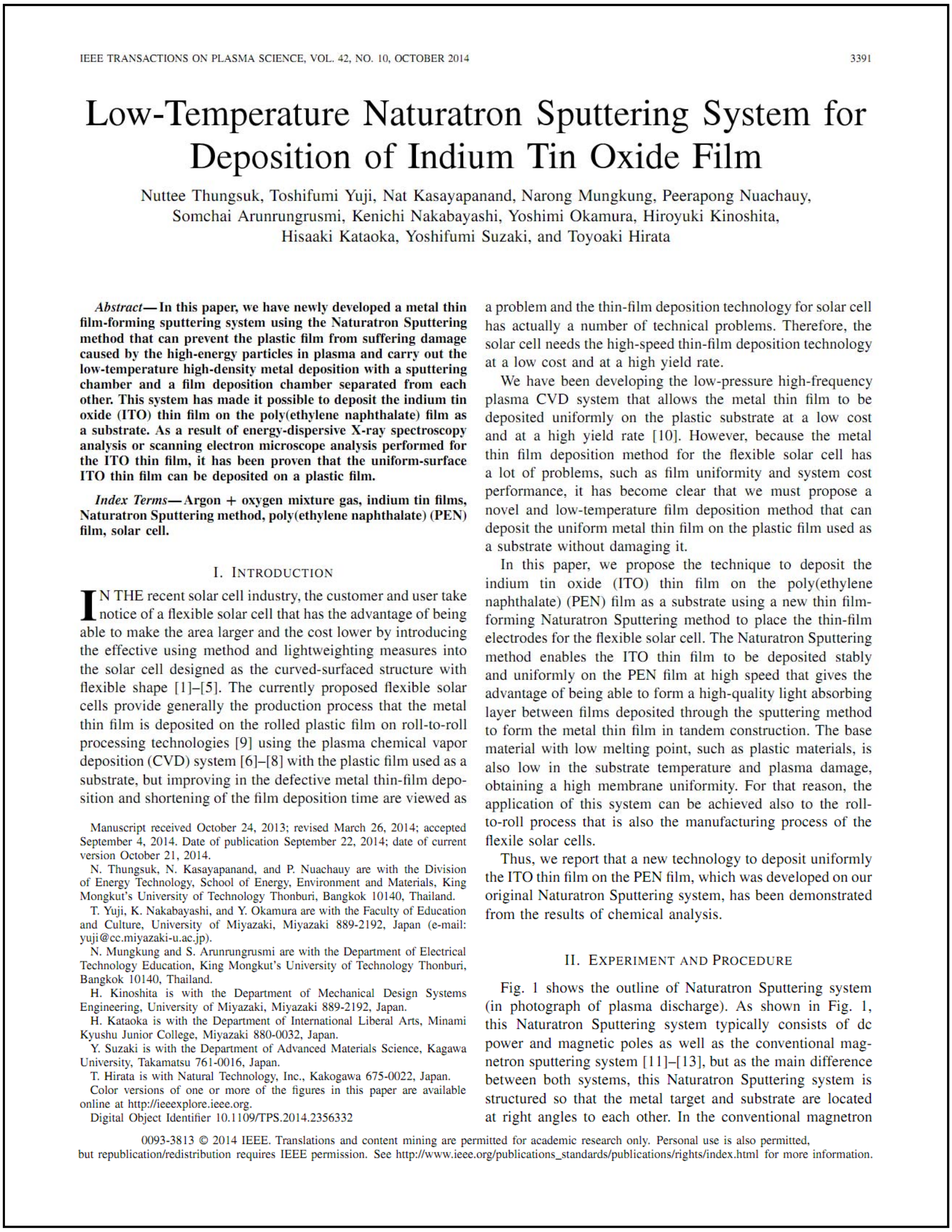

IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 42, NO. 10, OCTOBER 2014 3391

Low-Temperature Naturatron Sputtering System for Deposition of Indium Tin Oxide Film

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***Abstract*—In this paper, we have newly developed a metal thin film-forming sputtering system using the Naturatron Sputtering method that can prevent the plastic film from suffering damage caused by the high-energy particles in plasma and carry out the low-temperature high-density metal deposition with a sputtering chamber and a film deposition chamber separated from each other. This system has made it possible to deposit the indium tin oxide (ITO) thin film on the poly(ethylene naphthalate) film as a substrate. As a result of energy-dispersive X-ray spectroscopy analysis or scanning electron microscope analysis performed for the ITO thin film, it has been proven that the uniform-surface ITO thin film can be deposited on a plastic film.**

***Index Terms*—Argon + oxygen mixture gas, indium tin films, Naturatron Sputtering method, poly(ethylene naphthalate) (PEN) film, solar cell.**

I. INTRODUCTION

IN THE recent solar cell industry, the customer and user take notice of a flexible solar cell that has the advantage of being able to make the area larger and the cost lower by introducing the effective using method and lightweighting measures into the solar cell designed as the curved-surfaced structure with flexible shape [1]–[5]. The currently proposed flexible solar cells provide generally the production process that the metal thin film is deposited on the rolled plastic film on roll-to-roll processing technologies [9] using the plasma chemical vapor deposition (CVD) system [6]–[8] with the plastic film used as a substrate, but improving in the defective metal thin-film deposition and shortening of the film deposition time are viewed as a problem and the thin-film deposition technology for solar cell has actually a number of technical problems. Therefore, the solar cell needs the high-speed thin-film deposition technology at a low cost and at a high yield rate.

We have been developing the low-pressure high-frequency plasma CVD system that allows the metal thin film to be deposited uniformly on the plastic substrate at a low cost and at a high yield rate [10]. However, because the metal thin film deposition method for the flexible solar cell has a lot of problems, such as film uniformity and system cost performance, it has become clear that we must propose a novel and low-temperature film deposition method that can deposit the uniform metal thin film on the plastic film used as a substrate without damaging it.

In this paper, we propose the technique to deposit the indium tin oxide (ITO) thin film on the poly(ethylene naphthalate) (PEN) film as a substrate using a new thin film-forming Naturatron Sputtering method to place the thin-film electrodes for the flexible solar cell. The Naturatron Sputtering method enables the ITO thin film to be deposited stably and uniformly on the PEN film at high speed that gives the advantage of being able to form a high-quality light absorbing layer between films deposited through the sputtering method to form the metal thin film in tandem construction. The base material with low melting point, such as plastic materials, is also low in the substrate temperature and plasma damage, obtaining a high membrane uniformity. For that reason, the application of this system can be achieved also to the roll-to-roll process that is also the manufacturing process of the flexile solar cells.

Thus, we report that a new technology to deposit uniformly the ITO thin film on the PEN film, which was developed on our original Naturatron Sputtering system, has been demonstrated from the results of chemical analysis.

II. EXPERIMENT AND PROCEDURE

Fig. 1 shows the outline of Naturatron Sputtering system (in photograph of plasma discharge). As shown in Fig. 1, this Naturatron Sputtering system typically consists of dc power and magnetic poles as well as the conventional magnetron sputtering system [11]–[13], but as the main difference between both systems, this Naturatron Sputtering system is structured so that the metal target and substrate are located at right angles to each other. In the conventional magnetron

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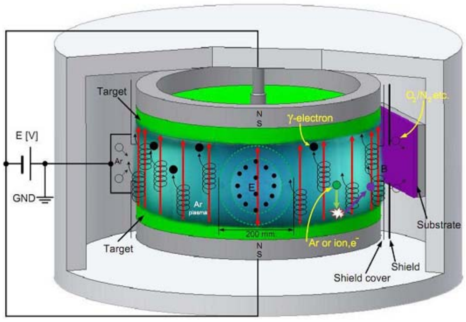

Fig. 1. Schematic of Naturatron Sputtering system. Inset: photograph of plasma discharge and molybdenum target.

sputtering system, the substrate existing in plasma has caused many problems that the temperature of substrate becomes higher, ion in plasma is resputtered, and the substrate electric potential is always structurally negative to repeat a collision between secondary electrons, which leads to an unusable plastic substrate and un-uniformed thin-film deposition. In the Naturatron Sputtering system, however, two targets are located directly opposite with the electric field and magnetic field kept parallel to each other between these targets, plasma is also confined between these targets, electrons move at high speed between them, while twining around lines of magnetic force, large current produces a high-density plasma at a low voltage, and only the atoms sputtered by a plasma-type gas ion are deposited on the substrate located at right angles to both targets. As a result, the magnetic field around each target is enhanced to improves the plasma density and also, the low-temperature (25 °C) thin-film deposition becomes possible because a little plasma damage occurs to the substrate, and its temperature is affected by only radiant heat in plasma. Further, a composition deviation of the thin film deposited on the substrate is not caused by the high-energy plasma-type gas particles resputtered. This means that the optimum film composition, which is the same as that of target, can be deposited uniformly on the front surface of substrate that is sensitive to damage. When using mixed gas (reactive gas) as plasma generating gas, the extremely high film deposition rate can be obtained by supplying the reactive gas from near the substrate and by making it react with the sputtered atoms.

The Naturatron Sputtering system has improved especially the following main features more than the conventional magnetron sputtering system.

1) The separation of a sputtering chamber from a film deposition chamber has decreased material damage, caused by the high-energy particles in plasma, and has improved the high-level reproducibility of film deposition.
2) The Naturatron Sputtering system has realized a film deposition speed by one-digit higher, at a high yield rate, than the conventional sputtering system.
3) Installation of the oxidizing chamber for sputtered material has remarkably improved the film deposition control.

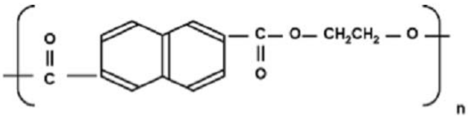

Fig. 2. Chemical structure model of the PEN film.

4) Because the film deposition chamber is hard to be affected by a plasma, the thin film has been allowed to be deposited on the plastic substrate even at the low temperature (less than 100 °C) of substrate in thin film deposition, which was impossible in the conventional sputtering system.

We propose the technique to, we used the 100 × 500 mm^2 ITO target (Sn: 5 wt%) and the Argon (50 sccm) and Oxygen (1.5 sccm) mixture gas as plasma generating gas for thin-film deposition. The specifications of thin-film deposition are as follows: 145 nm/min film deposition rate, 1.3 kW plasma input power, the target voltage was 500 V 2500 s film deposition time, 25 mT central magnetic field strength, 100 °C thin-film depo sition temperature, and 5.6 × 105 Pa ultimate gas pressure. As the basic study in this system so far, when set the plasma 127 making electric power 2.0 kW by Ar$^+$ O$_2$ in the Si target, the production membrane of SiO$_2$ is obtaining the high-speed production membrane property of 150 nm/min. Likewise, as to the distance between the target and the substrate, when narrowing the distance, the piece number of incidence of the supper atoms against the substrate increases, resulting in the production membrane rate getting faster. Accordingly, the radiant heat of plasma rises, and the substrate temperature also rises. As a result of the fact that the distance between the target and the substrate that is the optimum in the plastic material was found, we determined 174 mm, which is difficult to give damage without melting the plastic material.

Since this high-speed film deposition allows the atoms sputtered from the target to react effectively with the radicals produced by the reactive gas, it prevents the oxide accumulation on the surface of target, the reduction of deposition rate, and the frequent occurrence of defective arc.

Fig. 2 shows the structural formula of the PEN film (Teijin Dupont Films, Q51) as a plastic substrate and 51 μm in thickness (height: 210 mm and width: 297 mm) used for thin-film deposition. As the main features of PEN film, it has excellent heat resistance and mechanical characteristics. The PEN film was exposed to target at 174 mm from on substrate. We are aiming at depositing the ITO thin film on the PEN film to use them as the electrode (positive) material for the flexible solar cell.

The crystal structure of the surface and cross section of the ITO thin film that was deposited on the plastic substrate according to the Naturatron Sputtering system was observed visually by the focused ion beam (FIB) scanning electron microscope (SEM) (HITACHI High-Technologies: FIB-2100). In addition, the elemental and composition analyses were conducted for the surface of ITO thin film by the

Fig. 3. Photograph of FIB–SEM images (ITO on PEN film).

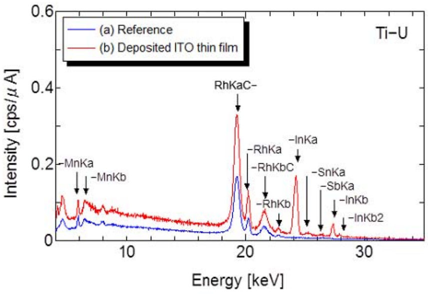

Fig. 4. EDX Ti–U spectrums in the region.

energy-dispersive X-ray spectroscopy (EDX) analysis method and the fundamental parameter (FP) method [14], respectively.

III. Results and Discussion

Fig. 3 shows the SEM image that the cross section of ITO thin film was observed, while the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was being shaved off by the FIB–SEM. As shown in Fig. 3, it can be confirmed that approx. 145-nm ITO thin film is deposited on the PEN film and the crystal structure of the deposited ITO thin film surface is kept uniform. Likewise, as a result of having measured the step difference profile from the surface profiler systems (AlphaStep D-100), the ITO thin film of 145 nm in the membrane thickness on the PEN film has been formed a film, we ascertained that the surface roughness is also lower than 0.39 nm or less.

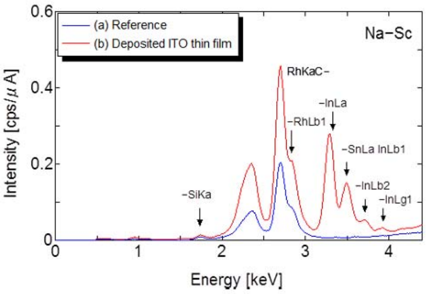

Fig. 5. EDX Na–Sc spectrums in the region.

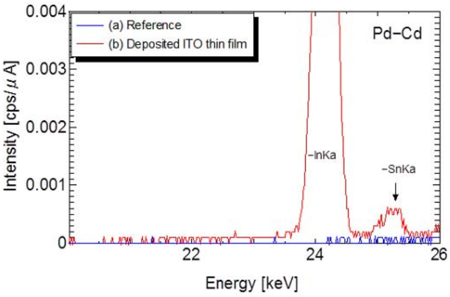

Fig. 6. EDX Pd–Cd spectrums in the region.

Fig. 4 shows the qualitative analysis of Ti–U spectrum that the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was measured using the FP method and the EDX analysis method. As shown in Fig. 4, the spectrum (a) is the qualitative analysis of spectrum measured as an undeposited reference (sample) film. When making a comparison between the spectrums (a) and (b), the latter indicates remarkably the peak points of -Inka, -SnKa, -InKb, and -Inkb2. These results are based on the qualitative analysis of all components of ITO.

Fig. 5 shows the qualitative analysis of Na–Sc spectrum that the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was measured using the EDX analysis method. Besides Fig. 4, the spectrum (a) shows a reference film in Fig. 5. When making a comparison between the spectrums (a) and (b), the latter indicates remarkably the peak points of -InLa, -SnLa InLb1, -InLb2, and -LnLg1. Besides Fig. 4, these results are also based on the qualitative analysis of all components of ITO.

Fig. 6 shows the qualitative analysis of Pd–Cd spectrum that the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was measured using the FP method and the X-ray spectra (EDX) analysis method. Besides Fig. 4, the spectrum (a) shows a reference film in Fig. 6. When making a comparison between the spectrums (a) and (b), the latter indicates remarkably the peak points of -InKa and -SnKa. These results are based on the qualitative analysis of all components of PEN film. Information on element analysis of spectrum for the PEN film is deleted in the spectrum (b) because the ITO thin film is deposited on the PEN film as a plastic substrate.

Fig. 7 shows the qualitative analysis of C1 spectrum that the surface of ITO thin film, deposited according to the Naturatron

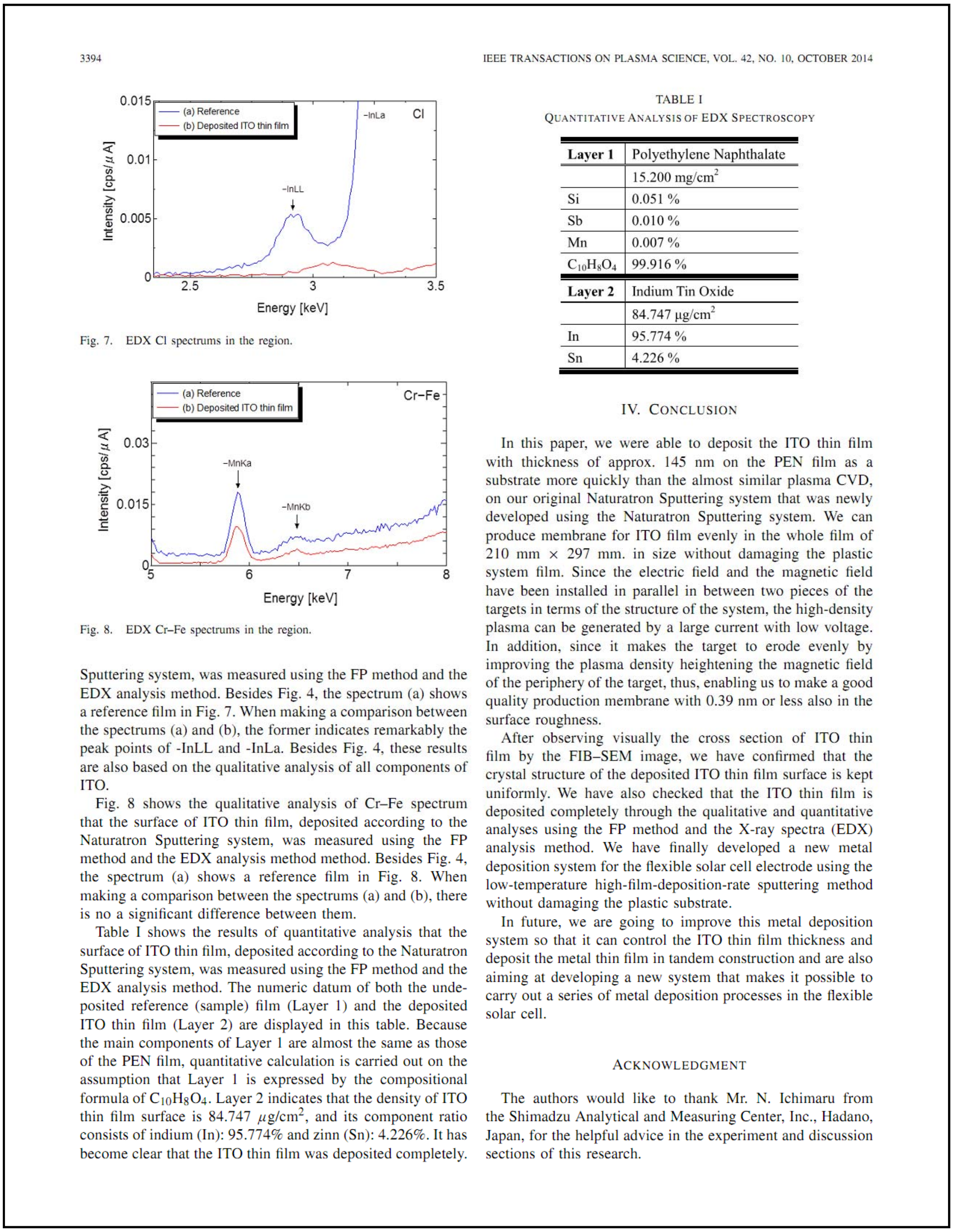

Fig. 7. EDX Cl spectrums in the region.

Fig. 8. EDX Cr–Fe spectrums in the region.

Sputtering system, was measured using the FP method and the EDX analysis method. Besides Fig. 4, the spectrum (a) shows a reference film in Fig. 7. When making a comparison between the spectrums (a) and (b), the former indicates remarkably the peak points of -InLL and -InLa. Besides Fig. 4, these results are also based on the qualitative analysis of all components of ITO.

Fig. 8 shows the qualitative analysis of Cr–Fe spectrum that the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was measured using the FP method and the EDX analysis method method. Besides Fig. 4, the spectrum (a) shows a reference film in Fig. 8. When making a comparison between the spectrums (a) and (b), there is no a significant difference between them.

Table I shows the results of quantitative analysis that the surface of ITO thin film, deposited according to the Naturatron Sputtering system, was measured using the FP method and the EDX analysis method. The numeric datum of both the undeposited reference (sample) film (Layer 1) and the deposited ITO thin film (Layer 2) are displayed in this table. Because the main components of Layer 1 are almost the same as those of the PEN film, quantitative calculation is carried out on the assumption that Layer 1 is expressed by the compositional formula of $C_{10}H_8O_4$. Layer 2 indicates that the density of ITO thin film surface is 84.747 μg/cm^2, and its component ratio consists of indium (In): 95.774% and zinn (Sn): 4.226%. It has become clear that the ITO thin film was deposited completely.

TABLE I

QUANTITATIVE ANALYSIS OF EDX SPECTROSCOPY

Layer 1	Polyethylene Naphthalate
	15.200 mg/cm^2
Si	0.051 %
Sb	0.010 %
Mn	0.007 %
$C_{10}H_8O_4$	99.916 %
Layer 2	Indium Tin Oxide
	84.747 µg/cm^2
In	95.774 %
Sn	4.226 %

IV. CONCLUSION

In this paper, we were able to deposit the ITO thin film with thickness of approx. 145 nm on the PEN film as a substrate more quickly than the almost similar plasma CVD, on our original Naturatron Sputtering system that was newly developed using the Naturatron Sputtering system. We can produce membrane for ITO film evenly in the whole film of 210 mm × 297 mm. in size without damaging the plastic system film. Since the electric field and the magnetic field have been installed in parallel in between two pieces of the targets in terms of the structure of the system, the high-density plasma can be generated by a large current with low voltage. In addition, since it makes the target to erode evenly by improving the plasma density heightening the magnetic field of the periphery of the target, thus, enabling us to make a good quality production membrane with 0.39 nm or less also in the surface roughness.

After observing visually the cross section of ITO thin film by the FIB–SEM image, we have confirmed that the crystal structure of the deposited ITO thin film surface is kept uniformly. We have also checked that the ITO thin film is deposited completely through the qualitative and quantitative analyses using the FP method and the X-ray spectra (EDX) analysis method. We have finally developed a new metal deposition system for the flexible solar cell electrode using the low-temperature high-film-deposition-rate sputtering method without damaging the plastic substrate.

In future, we are going to improve this metal deposition system so that it can control the ITO thin film thickness and deposit the metal thin film in tandem construction and are also aiming at developing a new system that makes it possible to carry out a series of metal deposition processes in the flexible solar cell.

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REFERENCES

[1] K. Moriwaki *et al.*, "Monolithically integrated flexible Cu(In,Ga)Se_2 solar cells and submodules using newly developed structure metal foil substrate with a dielectric layer," *Solar Energy Mater. Solar Cells*, vol. 112, pp. 106–111, May 2013.

[2] M. Jørgensen, K. Norrman, and F. C. Krebs, "Stability/degradation of polymer solar cells," *Solar Energy Mater. Solar Cells*, vol. 92, no. 7, pp. 686–714, 2008.

[3] X. Huang *et al.*, "Stainless steel mesh-based flexible quasi-solid dye-sensitized solar cells," *Solar Energy Mater. Solar Cells*, vol. 94, no. 6, pp. 1005–1010, 2010.

[4] G. Hashmi *et al.*, "Review of materials and manufacturing options for large area flexible dye solar cells," *Renew. Sustain. Energy Rev.*, vol. 15, no. 8, pp. 3717–3732, 2011.

[5] X. Mathew, J. P. Enriquez, A. Romeo, and A. N. Tiwari, "CdTe/CdS solar cells on flexible substrates," *Solar Energy*, vol. 77, no. 6, pp. 831–838, 2004.

[6] H. Sonobe, A. Sato, S. Shimizu, T. Matsui, M. Kondo, and A. Matsuda, "Highly stabilized hydrogenated amorphous silicon solar cells fabricated by triode-plasma CVD," *Thin Solid Films*, vol. 502, nos. 1–2, pp. 306–310, 2006.

[7] J. K. Rath *et al.*, "Recent advances in very high frequency plasma enhanced CVD process for the fabrication of thin film silicon solar cells," *Thin Solid Films*, vol. 517, no. 17, pp. 4758–4761, 2009.

[8] M. Jurzecka, S. Kluska, S. Jonas, H. Czternastek, and K. Zakrzewska, "RF PE CVD deposition of amorphous a-Si_xN_y:H layers for application in solar cells," *Vacuum*, vol. 82, no. 10, pp. 1128–1132, 2008.

[9] N. Espinosa *et al.*, "Life cycle assessment of ITO-free flexible polymer solar cells prepared by roll-to-roll coating and printing," *Solar Energy Mater. Solar Cells*, vol. 97, pp. 3–13, Feb. 2012.

[10] T. Yuji *et al.*, "Surface modification of Si wafer by low-pressure high-frequency plasma chemical vapor deposition method," *IEEE Trans. Plasma Sci.*, vol. 39, no. 6, pp. 1427–1431, Jun. 2011.

[11] S. Karthikeyan, A. E. Hill, J. S. Cowpe, and R. D. Pilkington, "The influence of operating parameters on pulsed D.C. magnetron sputtering plasma," *Vacuum*, vol. 85, no. 5, pp. 634–638, 2010.

[12] C.-H. Park, Y.-K. Kim, S.-H. Lee, W.-G. Lee, and Y.-M. Sung, "Surface-discharge characteristics of MgO-thin films prepared by reactive RF unbalanced magnetron sputtering," *Thin Solid Films*, vol. 366, nos. 1–2, pp. 88–94, 2000.

[13] L. Pekker, "Plasma chemistry model of DC magnetron reactive sputtering in Ar–O_2 gas mixtures," *Thin Solid Films*, vol. 312, nos. 1–2, pp. 341–347, 1998.

[14] V. Y. Borkhodoev, "Accuracy of the fundamental parameter method for X-ray fluorescence analysis of rocks," *X-Ray Spectrometry*, vol. 31, no. 3, pp. 209–218, 2002.

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The Development of Polyethylene Naphthalate Films by Low-pressure High-frequency Plasma Chemical Vapor Deposition System with Advance Oxidations Process

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Abstract:

The low-pressure high-frequency plasma chemical vapor deposition (CVD) system was developed with non-thermal plasma process to study the Polyethylene naphthalate (PEN) surface characteristics. Plasma surface treatment by oxygen can improve the adhesive properties. A mixture of Ar and O_2 gas was used in the plasma treatment. The oxygen gas flow rate was between 0.1 L/min and 0.5 L/min, whereas the Ar gas flow rate was set at 10 L/min. The surface was investigated by contact angle meter and X-ray photoelectron spectroscopy (XPS) to determine the differences between untreated and treated surfaces. The results indicated that the low-pressure high-frequency plasma chemical vapor deposition system could be used for surface modification.

Keywords: Plasma CVD, Argon+Oxygen mixture gas, Flexible solar cell, Surface treatment, PEN films

Introduction

Solar cell manufacturers are currently searching for ways to reduce the cost of production and increase the production scale for silicon-based solar cells (1). Most commercial silicon-based solar panels are categorized into two types: monocrystalline and poly-crystalline. They have comparatively higher efficiencies than other types of solar panels. However, there are challenges in some aspects, such as a complicated manufacturing process, heavy material and a high overall cost (2). Silicon-based thin-film solar cells have lighter weight compared to mono-crystalline and polycrystalline cells, but they have lower efficiency. The cost of silicon-based solar panels depends on the processing. In other words, the more complex the process is, the higher the cost is. In response to these challenges, solar sell manufacturers are simplifying the manufacturing process, which will gradually lower the cost.

Polyethylene naphthalate (PEN) films are plastic, which is light-weight and flexible therefore its characteristics is suitable for substrate material of electronic parts. The solar cell market has a demand for low cost, thus the new generation of solar cell has a tendency to use plastic substrate material, plastic is light-weight which results in low cost transportation, roll -to-roll (R2R) technology production for solar cell can be used (3).

At present, ZnO has been intensively researched due to the advantageous features and suitability such as, a wide band gap semiconductor (3.3 eV at room temperature), direct band gap, attention of physical and chemical properties (4-5). Besides, ZnO has been applied in solar cells (6). Transparent ZnO conducting electrodes can be coated with a polymer surface (7). However, due to the poor adhesive characteristics of the polymer, the surface has to be modified (8). Modifying the surface using oxygen surface treatment can improve adhesion on the polymer surface (9) with results in increased efficiency of this solar cell.

The polymer material can be destroyed by high temperatures, so plasma surface treatment must be performed at low temperatures (10). Plasma phenomena incur advance oxidation process due to many reactions during plasma deposition such as etching, chain scission, cross-linking and radicals. In generally, it is

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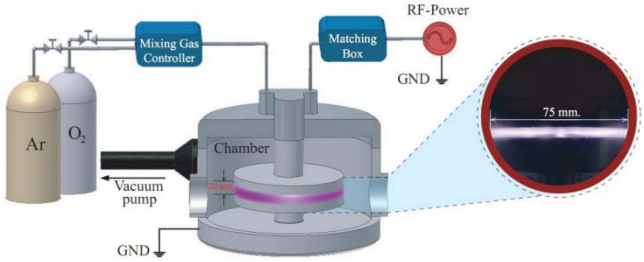

Figure 1. The schematic diagram of the experimental setup and photograph during plasma deposition.

difficult to coat metal film on plastic. Therefore, the surface treatment by plasma processing was used to perform with oxidation phenomena. Consequently, substrate can be high adhesion between plastic surface and metal film. In addition, plasma chemical vapor deposition (CVD) has good characteristics in terms of uniform film formation, and most of all, is non-thermal plasma deposition (11-12). Thus, this plasma system is suitable for polymer materials.

In this paper, low-pressure high-frequency plasma chemical vapor deposition (CVD) system was developed with non-thermal plasma process to study the PEN surface characteristics. After oxygen plasma surface treatment, the surface was investigated by using a contact angle meter and X-ray photoelectron spectroscopy (XPS) to describe the changes in the film characteristics. The changes of the PEN surface characteristics could be applied on the ZnO surface coating.

Experimental Setup

Figure 1 shows the system of low-pressure high-frequency plasma chemical vapor deposition used for this research. The main components of the plasma CVD system are the chamber, mass flow controller, RF-power and matching box, vacuum pump and gas supply. The vacuum chamber of the plasma CVD system was composed of stainless steel (SUS316), which was 430 mm in diameter and 180 mm in height. The plasma electrode for generating the plasma process was 200 mm in diameter, and the distance between the upper and lower plasma electrodes was maintained at 20 mm. The showerhead and gas distribution plate had 145 fine pores arranged in the shape of a grid. The distance between each pore was 12 mm, and each pore had a diameter of 1.0 mm.

The electrode has a structure that allows for the formation of a uniform thin film and uses vapor to form a metallic thin film at low temperature. A substrate heater was built in the lower electrode in the vacuum chamber of plasma CVD system, which allowed the device to perform tandem construction of the thin-film for annealing. The port for exhaust gas, which was a fundamental structure in the plasma equipment, was installed in the vacuum chamber at the side of the system surface. Inside, the vacuum chamber was maintained at a constant temperature during plasma deposition by flowing cool water onto the outer wall portion of the reactor of the vacuum chamber.

125μm-thick PEN films (Teijin DuPont: Q51) were used in this experiment. A mixture of Ar and O_2 gas was used to study the PEN film surface characteristics after completion of the surface treatment. The argon gas flow rate was kept at 10 L/min, and the oxygen gas flow rate was varied from 0.1 to 0.5 L/min to mix with the argon gas. It took 5.0 min for the surface treatment to be completed. The pressure in the vacuum chamber during the plasma surface treatment processing was 3.2×10^2 Pa. The temperature in the vacuum room was maintained below 30°C during the surface treatment by using water cooling of the plasma chamber which did not cause heat during plasma deposition so that PEN films could not be destroyed. A13.56 MHz of frequency and 300 W of RF-power were used for this experiment to apply different gases on the substrate. The lower electrode served as a grounded one. The inset of Fig 1.shows a photograph of the plasma phenomenon(20 mm between the upper and lower plasma electrodes) under the conditions of 300 W plasma power, 3.2×10^2 Pa vacuum level, 10 L/min Ar flow rate and 0.5 L/min O_2 flow rate.

After the treatment of the PEN surface, the surface was investigated using X-ray photoelectron spectroscopy (XPS) with a Shimadzu/KRATOS, AXIS-HS and a Kyowa Interface Science Co., Ltd (Type CA-D) contact angle meter. The contact angle meter was used

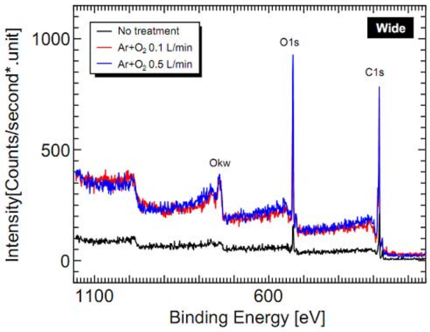

Figure 2. XPS wide scan spectra on PEN surface.

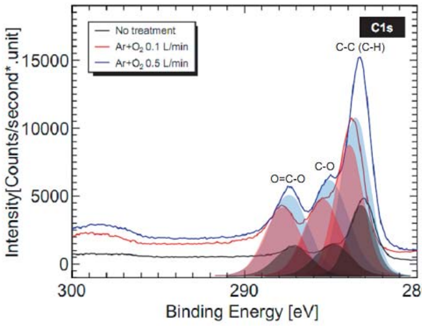

Figure 3. XPS C1s scan spectra on the PEN surface.

to study the hydrophilic properties of the PEN surface after plasma treatment by using the sessile drop method, which consisted of dropping 1.0 µL pure water droplets (13). The surface of the PEN was thoroughly investigated and chemically analyzed by C1s and O1s elemental analysis using XPS with a Mg kα (1253.6 eV) X-ray source.

Results and Discussion

Figure 2 shows the wide scan spectrum obtained by the narrow scanning spectrum method when measured by XPS, after plasma surface treatment with the untreated and treated surface by low-pressure high-frequency plasma chemical vapor deposition system for mixing Ar gas and O_2gas, when Ar gas was supplied at a 10 L/min flow rate and O_2 gas was supplied at a 0.1 and 0.5 L/min flow rate. It could be confirmed from O(KW), O1s and C1s radical by comparing the spectrum in this figure. The intensity of O1s and C1s peaks in case of untreated condition ware 164 and 211 counts/second*.unit, respectively. While surfaces ware treated with the mixture of Ar and O_2 gas 0.1 L/min flow rate by low pressure high frequency plasma chemical vapor deposition system, the intensity of O1s and C1s peaks ware increased 762 and 730 counts/second*.unit, respectively, and intensity of O1s and C1s peaks ware increased 929 and 784 counts/second*.unit, respectively when O_2 gas flow rate was 0.1 L/min. It could be confirmed that the radicals formation from this plasma system with intensity difference of O1s and C1s peaks in case of untreated and treated condition with various O_2 flow rate. The O_2 gas mixture during plasma deposition process incurred spectrum change from observed the intensity of radicals were increased, the radicals were generated in this plasma process and those radicals caused PEN surface modification.

Figure 3 shows the C1s high-resolution spectrum obtained by the narrow scanning spectrum method when measured by XPS under the same experimental conditions as in Figure 2. This figure shows three spectrum lines and curve-fitting using a Gaussian-type distribution with the untreated and treated surface. Each spectrum of C1s investigated by XPS decomposed into 3 component peaks (C-H, C-O and O-C=O) under different experimental conditions. It could be confirmed that C-H (in the vicinity of 283-284 eV), C-O (in the vicinity of 285-286 eV), and O-C=O (in the vicinity of 287-288 eV) (14-15). It was found that the spectrum peaks under the three conditions showed significant differences; the lowest spectrum peak was the untreated surface, and the highest spectrum peak was the surface treated by the low-pressure high-frequency plasma CVD system with a mixture of Ar gas and O_2 gas with the O_2 gas flow rate at 0.5 L/min, which percentage between untreated and treated differed about 30.6% - 68%. An increased O_2 flow in the low-pressure high-frequency plasma CVD system caused radical generation as a result of the dissociation of atoms, ions, and gas molecules and caused reactions to occur on the surface. The vital characteristics of the modification of the surface were due to O radicals adhering on the PEN surface, and those molecules were chemically bonded on the surface, while the surface was maintained.

Figure 4 shows the effect of O_2 gas flow rate when black line is the relationship between the O_2 gas flow rate and the contact angle and the action of a water droplet when dropped onto the PEN surface, with the measurement from the contact angle meter using the sessile drop method and 1.0 µL pure water droplets. The angle of the water droplet when the Ar gas flow rate was 10 L/min was 51.5 degrees, and the contact angle decreased to 15.3, 10.3 and 6.3 degrees when

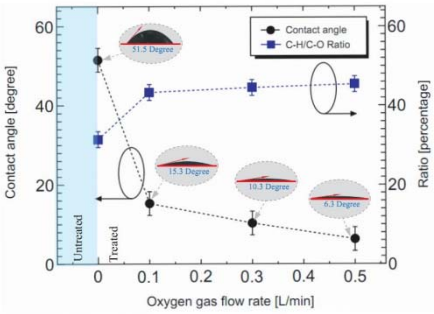

Figure 4. The effect of O_2 gas flow rate.

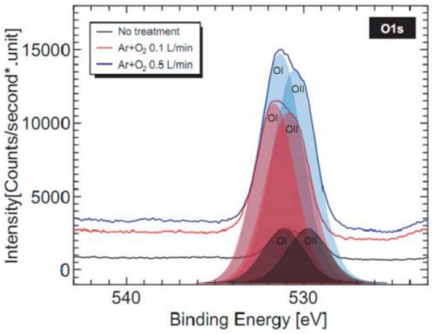

Figure 5. XPS O1s scan spectra on the PEN surface.

the O_2 gas flow rate was 0.1, 0.3 and 0.5 L/min, respectively, while Ar gas flow rate was maintained at 10 L/min. The angle of the water droplet decreased on the PEN substrate as the O_2 gas flow rate in the plasma CVD system increased, which results in dissociation of the gas plasma being enhanced in the plasma region. Additionally, the dissociation of oxygen also generated radicals. In addition, the ratio of C-H/C-O shows in blue line of this Figure was approximately 31%, 43%, 44% and 45% for the untreated condition and the plasma surface treatment with an O_2 gas flow rate at 0.1, 0.3 and 0.5 L/min, respectively, with the Ar gas flow rate at 10 L/min. It was found that during the angle of the water droplet decreased and the ratio of C-H/C-O increased when O_2 gas flow rate increased in this system. The radical formation by the low-pressure high-frequency plasma CVD system was considered to affect the relationship of the changing of contact angle. This radical was reformed at the PEN surface, which resulted in changes in the hydrophilic properties and radical species after the plasma surface treatment on the PEN surface. Therefore, the hydrophilic properties were improved by increasing the oxygen gas flow rate, resulting in OH radical generation and bonding with the chemical structure of the PEN surface.

Figure 5 shows the O1s high-resolution spectrum obtained by the narrow scanning spectrum method when measured by XPS under the same experimental conditions as in Figure 2 The O1s decomposed into 2 components of O-C and O=C at the OI and OII component, respectively, under the untreated and treated surface conditions (16). The O1s spectrum had the composition of OI and OII in the vicinity of 531.5 eV and 530.5 eV, respectively, for the mixtures of Ar and O_2 gas. In addition, the spectrum of O1s from the untreated condition had the composition of OI and OII in the vicinity of 531 eV and 530eV, respectively. The O1s spectrum peak increased approximately 2,500, 12,000 and 15,000 counts/second*.unit for the untreated condition and treated surface with an O_2 gas flow rate at 0.1 and 0.5 L/min, respectively. The percentage between untreated and treated differed about 72% - 82%. The changes of the O1s spectrum were due to radical formation by the low-pressure high-frequency plasma CVD method, which resulted in influence of electrons and O radicals being activated and causing reactions on the PEN structure with chemical bonds.

The C-O, O=C and O-C=O bonds which are the functional groups were generated by oxidation of surface (17). It was found that oxidation groups were increased from investigation by C1s and O1s by XPS analysis. The oxidation groups changed very differently during untreated and treated condition by the low-pressure high-frequency plasma CVD method on PEN surface. On the other hand the oxidation groups changed slightly when the oxygen gas flow rate was increased on this system, radicals could not be easily attacked and creped in order to create bonds in PEN surface.

Figure 6 a) shows the model of the phenomenon of the plasma surface treatment on the PEN substrate by the low-pressure high-frequency plasma CVD system, and Figure 6 b) shows new chemical structure of the PEN film after oxygen surface treatment. The introduction of oxygen gas into the plasma gas resulted in increased ionization due to electron impact with oxygen atoms in the plasma by reaction (1).Those electrons impacted molecules, atoms and ions, which resulted in excitation and dissociation by reactions (2)-(5).The electron impact of atoms and molecules in a plasma was the most important process of ionization excitation and dissociation. In addition, the O atoms

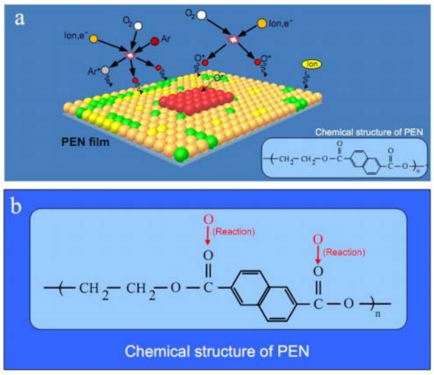

Figure 6. Illustration of the low-pressure high-frequency plasma CVD on the PEN surface.
a) Mechanism of oxygen plasma surface treatment.
b) Chemical structure of the PEN film after oxygen plasma surface treatment.

and O radicals were produced following reactions (1)-(5) (18-21).

$$e + O_2 \rightarrow e + O_2^+ + e \tag{1}$$

$$e + O_2^+ \rightarrow O + O \tag{2}$$

$$e + O \rightarrow e + O^* \tag{3}$$

$$e + O_2 \rightarrow e + O + O \tag{4}$$

$$e + Ar + O_2 \rightarrow Ar^* + O + O^* \tag{5}$$

It can be assumed that oxygen radicals cause the PEN surface changes and difference from original surface, thus producing a oxygen doping effect. Usually, O_2^+ and O radical species (O_2* and O*) are generated in the gas phase of plasma chemical vapor deposition (22). As the functional groups on the PEN film surface were destroyed as a result of dissociate of oxygen molecules, oxygen atoms and electrons, and it reacted with functional groups on the surface. Under the influence of complementary radicals in the plasma, the structure of the molecules on the surface of PEN was changed. The radicals increment from plasma treatment caused the PEN films structure was changes, with results in efficiency of DSSCs higher when compared with untreated condition (23).

Conclusion

The surface treatment was successfully performed by the low-pressure high-frequency plasma CVD system. The results were investigated by measuring the PEN surface characteristics. From the investigation, an increase in the oxygen flow rate resulted in improved hydrophilic properties, as seen from the measurements with the contact angle meter. The contact angle decreased, confirming the formation of radicals on the PEN surface as a result of the surface treatment by the low-pressure high-frequency plasma chemical vapor deposition system. The wide scan, C1s and O1s XPS spectra confirmed the radical formation on the PEN surface caused by surface treatment with this system. Therefore, radical creation was a result of electron and ion breakdown and a combination of oxygen gas in the plasma process. Only these radical could change the surface of the PEN by adhering and increasing the O radicals on the surface with advance oxidations process from this system developed while maintaining the original structure of the PEN. The oxidations process was performed by plasma processing. As the results, the contact angle and ratio of C-H/C-O was decreased and increased, respectively. Therefore, surface treatment using the low-pressure high-frequency plasma CVD system on the PEN surface increased the O radicals, resulting in increased surface adhesion properties. In addition, the low-pressure high-frequency plasma CVD system cannot melt or destroy the PEN films due to this system could not generate heat during plasma surface treatment.

The changes of the PEN surface properties were understood from the investigation. Therefore, our crucial challenge in the future is development and formation of ZnO films on plastic substrate by developing high-frequency low-pressure plasma CVD system for next generation of solar cell industry.

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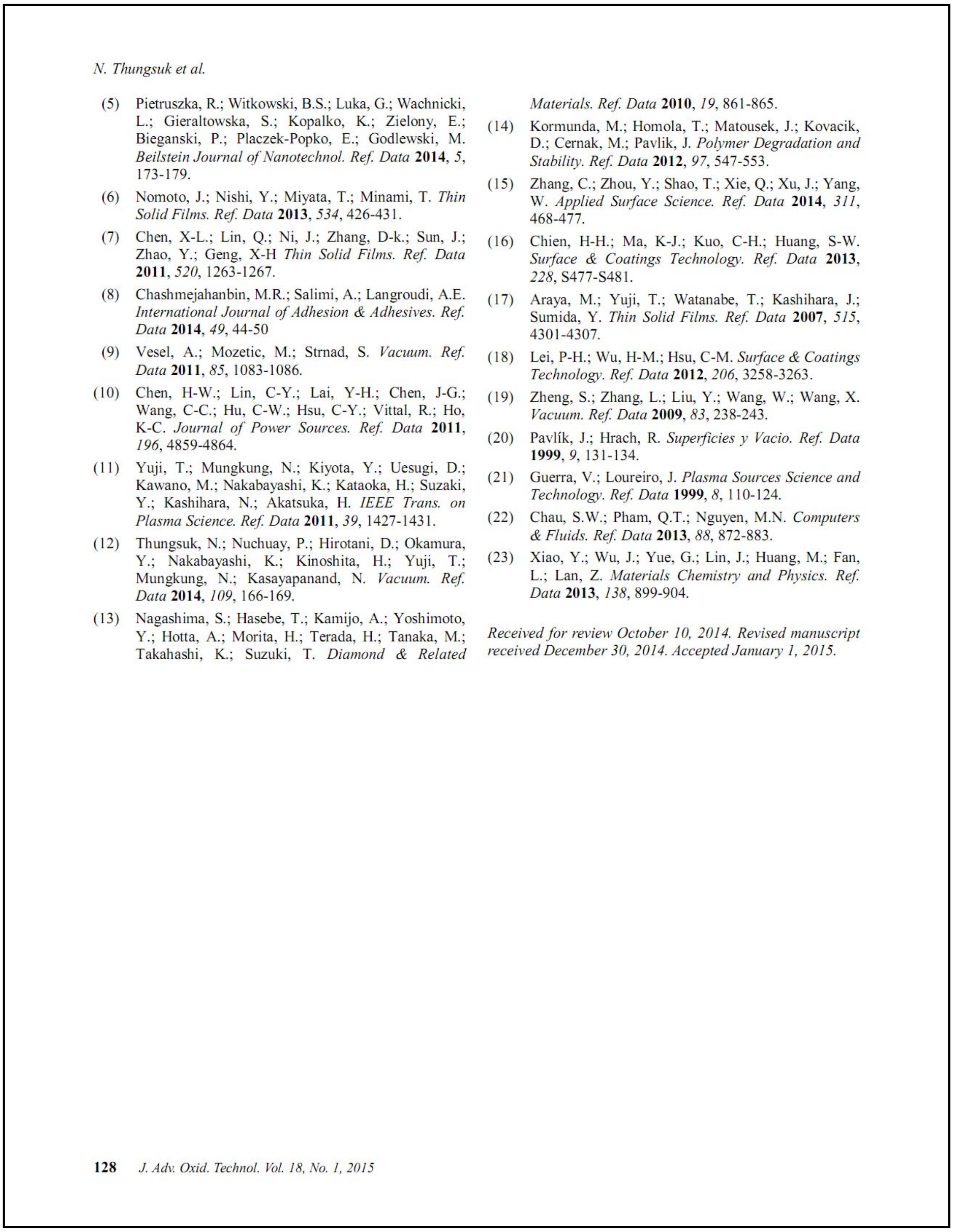
Reference

(1) Tyagi, V.V.; Rahim, N.A.A.; Rahim, N.A.; Selvaraj, J.A.L. *Renewable and Sustainable Energy Reviews. Ref. Data* **2013**, *20*, 443-461.

(2) Gong, J.; Liang, J.; Sumathy, K. *Renewable and Sustainable Energy Reviews. Ref. Data* **2012**, *16*, 5848-5860.

(3) Dupont, S.R.; Oliver, M.; Krebs, F.C.; Dauskardt, R.H. *Solar Energy Materials & Solar Cells. Ref. Data* **2012**, *97*, 171-175.

(4) Martín, A.; Espinós, J.P.; Justo, A.; Holgado, J.P.; Yubero, F.; González-Elipe, A.R. *Surface and Coatings Technology. Ref. Data* **2002**, *151-152*, 289-293.



(5) Pietruszka, R.; Witkowski, B.S.; Luka, G.; Wachnicki, L.; Gieraltowska, S.; Kopalko, K.; Zielony, E.; Bieganski, P.; Placzek-Popko, E.; Godlewski, M. *Beilstein Journal of Nanotechnol. Ref. Data* **2014**, *5*, 173-179.

(6) Nomoto, J.; Nishi, Y.; Miyata, T.; Minami, T. *Thin Solid Films. Ref. Data* **2013**, *534*, 426-431.

(7) Chen, X-L.; Lin, Q.; Ni, J.; Zhang, D-k.; Sun, J.; Zhao, Y.; Geng, X-H *Thin Solid Films. Ref. Data* **2011**, *520*, 1263-1267.

(8) Chashmejahanbin, M.R.; Salimi, A.; Langroudi, A.E. *International Journal of Adhesion & Adhesives. Ref. Data* **2014**, *49*, 44-50

(9) Vesel, A.; Mozetic, M.; Strnad, S. *Vacuum. Ref. Data* **2011**, *85*, 1083-1086.

(10) Chen, H-W.; Lin, C-Y.; Lai, Y-H.; Chen, J-G.; Wang, C-C.; Hu, C-W.; Hsu, C-Y.; Vittal, R.; Ho, K-C. *Journal of Power Sources. Ref. Data* **2011**, *196*, 4859-4864.

(11) Yuji, T.; Mungkung, N.; Kiyota, Y.; Uesugi, D.; Kawano, M.; Nakabayashi, K.; Kataoka, H.; Suzaki, Y.; Kashihara, N.; Akatsuka, H. *IEEE Trans. on Plasma Science. Ref. Data* **2011**, *39*, 1427-1431.

(12) Thungsuk, N.; Nuchuay, P.; Hirotani, D.; Okamura, Y.; Nakabayashi, K.; Kinoshita, H.; Yuji, T.; Mungkung, N.; Kasayapanand, N. *Vacuum. Ref. Data* **2014**, *109*, 166-169.

(13) Nagashima, S.; Hasebe, T.; Kamijo, A.; Yoshimoto, Y.; Hotta, A.; Morita, H.; Terada, H.; Tanaka, M.; Takahashi, K.; Suzuki, T. *Diamond & Related Materials. Ref. Data* **2010**, *19*, 861-865.

(14) Kormunda, M.; Homola, T.; Matousek, J.; Kovacik, D.; Cernak, M.; Pavlik, J. *Polymer Degradation and Stability. Ref. Data* **2012**, *97*, 547-553.

(15) Zhang, C.; Zhou, Y.; Shao, T.; Xie, Q.; Xu, J.; Yang, W. *Applied Surface Science. Ref. Data* **2014**, *311*, 468-477.

(16) Chien, H-H.; Ma, K-J.; Kuo, C-H.; Huang, S-W. *Surface & Coatings Technology. Ref. Data* **2013**, *228*, S477-S481.

(17) Araya, M.; Yuji, T.; Watanabe, T.; Kashihara, J.; Sumida, Y. *Thin Solid Films. Ref. Data* **2007**, *515*, 4301-4307.

(18) Lei, P-H.; Wu, H-M.; Hsu, C-M. *Surface & Coatings Technology. Ref. Data* **2012**, *206*, 3258-3263.

(19) Zheng, S.; Zhang, L.; Liu, Y.; Wang, W.; Wang, X. *Vacuum. Ref. Data* **2009**, *83*, 238-243.

(20) Pavlík, J.; Hrach, R. *Superficies y Vacio. Ref. Data* **1999**, *9*, 131-134.

(21) Guerra, V.; Loureiro, J. *Plasma Sources Science and Technology. Ref. Data* **1999**, *8*, 110-124.

(22) Chau, S.W.; Pham, Q.T.; Nguyen, M.N. *Computers & Fluids. Ref. Data* **2013**, *88*, 872-883.

(23) Xiao, Y.; Wu, J.; Yue, G.; Lin, J.; Huang, M.; Fan, L.; Lan, Z. *Materials Chemistry and Physics. Ref. Data* **2013**, *138*, 899-904.

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Rapid communication

Development of low-pressure high-frequency plasma chemical vapor deposition method on surface modification of silicon wafer

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ABSTRACT

Even though silicon based solar cell currently has more efficient, the dye sensitized solar cell is considerably cheaper for manufacturing because of its low cost materials and simplicity process of fabrication. In this paper, the development of plasma formed equipments for thin film material on flexible solar cell using low-pressure high-frequency plasma chemical vapor deposition method on the surface of Si wafer with the mixture of Ar gas and O_2 gas is presented. The results indicate that using this method can be possible for surface modification.

In the present, renewable energy is the new energy which becomes more important for the world. There are many energy resources producing the renewable energy, for examples; wind, solar, and biomass. Solar cell is the most popular renewable energy due to its many advantages: sunshine can shine over all area so it is the largest energy source, and can be converted directly to various types of energy. The solar cell installation has been increasing in many countries in order to support for both industrial and household [1]. As solar cell installation increase, the solar cell industrial will increase too [2,3].

Recently, most of solar cell technology that use for commercial is silicon solar cell used for commercial e.g. Mono crystalline silicon solar cell, Poly crystalline silicon solar cell or Amorphous silicon solar cell. Due to the improving of development and efficiency continuously, but using of silicon technology in solar cell production for industrial is very complicated and high cost [4]. So the dye sensitized solar cell (DSSC) becomes more interesting nowadays because of its more efficient and higher power. Besides, it has light weight, easy to install, convenience for transportation, with various shapes [5–7]. The production of dye sensitized solar cell is not complicated with low cost, but in industrial, method has to find the method that suit for mass production. However, complexity of apparatus installation and solar cell production may cause many steps and too long time in huge amount of solar cell producing.

Roll to roll (R2R) technology has been improving for higher production capacity, lower weight and lower cost [8–10]. But, Mono crystalline silicon solar cell and poly crystalline silicon solar cell cannot be used with roll to roll technology due to solid material, due to roll to roll is suitable for flexible material. Owing to flexible material such as plastic or polymer can be used with substrate for flexible dye sensitized solar cell, this will results in conductive layer of plastic or polymer for flexible dye sensitized solar cell produces thin film with roll to roll technology. Flexible dye sensitized solar cell can be applied with roll to roll technology for higher production capacity with lower cost.

Plasma Physical Vapor Deposition (PVD) and plasma chemical vapor deposition (CVD) methods are normally used together to create thin film with good quality for solar cell industrial [11,12].

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The low temperature in plasma process is appropriate in using to generate a film for flexible solar cell to avoid damage of substrate [13–16], while plasma chemical vapor deposition has to appropriate for low temperature thin film formation, however, the low efficiency of dye sensitized solar cell have to be resolved. It was reported that using oxygen plasma treatment to conduct film can reduce the Oxygen vacancies and increase the dye absorption of dye sensitized solar cell. Those are a surface solar cell modification method for higher efficiency [17,18].

In this paper, we would like to present using plasma to surface modification of flexible dye sensitized solar cell by Oxygen plasma treatment under the condition of low-pressure high-frequency plasma chemical vapor deposition method with silicon wafer. We have developed plasma equipment and reduced steps of plasma measuring by investigating radicals and characters of surface after plasma treatment process by mixture Argon gas and Oxygen gas.

In this study, the plasma CVD system has deposition *on silicon wafer* surface treatment by generating low-pressure high-frequency. Fig. 1 shown the system of low-pressure high-frequency plasma chemical vapor deposition for this research. The chamber of plasma CVD system was composed of stain steel (SUS316), and this dimension was 430 mm and 180 mm diameter and high respectively. The plasma electrode for generate plasma process was 200 mm diameter. The distance between upper and lower plasma electrodes were set at 20 mm. The showerhead and gas distribution plate have 1.0 mm diameter hole with 145 fine pores arranged in the shape of grid, the distance between each hole was 12 mm; they are attached to the upper part of the electrode. The electrode has a structure that allows the formation of uniform thin film to be formed and using for spread the vapor to form a metallic thin film in low temperature plasma. The substrate heater has been built in the lower electrode in chamber of plasma CVD system, which make the device to carry out tandem construction of thin film formation for annealing. The port for gas exhaust, which is a fundamental structure in plasma equipment was installed in the chamber on the side surface of system. Inside the chamber was maintained at constant temperature during plasma deposition by flowing cooling water onto the outer wall portion of the reactor of chamber room.

We were used Ar gas and the mixture of Ar and O_2 gas to study characteristic of surface of silicon wafer. The flow rate of Ar gas was 10 L/min and various Oxygen gas 0.1–0.6 L/min to mix various oxygen gas together. The pressure of plasma CVD system was 2.4×10^2 Pa during plasma surface treatment on silicon wafer. Heat of substrate had been controlled at not over 30 °C working temperature by water cooled on plasma chamber. Frequency at 13.56 MHz and 300 W. RF-power were used for this experimental in applying to substrate with difference gases, while the lower electrode serves as a ground, it took surface treatment 10 min by a B-doped p-type Si (100) wafer.

Fig 1 shown the plasma emission of the electrode when mixture of Ar and O_2 gas were used as the plasma gas. This figure shows the phenomenon of plasma deposition on low-pressure high-frequency plasma CVD system when the scale between each plasma electrode is 20 mm. The inset shows photograph when taken from 75 mm width eyehole under the condition of plasma deposition with plasma power: 300 W, Vacuum level: 2.4×10^2 Pa, Ar flow rate: 10 L/min and O_2 flow rate: 0.3 L/min condition in plasma deposition. From plasma reaction observation in chamber room of low-pressure high-frequency plasma CVD system, the color of plasma during deposition process was violet color.

The surface treatment of B-doped p-type Si (100) wafer was investigated by using X-ray photoelectron spectroscopy (XPS) model Shimadzu/KRATOS; AXIS-HS and contact angle meter model Kyowa Interface Science Company; Type CA-D. We observed hydrophilic properties of B-doped p-type Si (100) wafer from contact angle meter after plasma treatment by using the $\theta/2$ method and consisted of dropping 1 μL pure water droplets. The surface of silicon wafer thoroughly investigated and chemical analyzed from the existence of C1s and O1s element using XPS with Mg kα(1253.6 eV) X-ray source. For the condition of experimental of surface treatment by plasma CVD system given in Table 1.

Fig. 2 shown the action of a water droplet dropped down onto a B-doped p-type Si (100) wafer with contact angle meter using the $\theta/2$ method and pure water droplets 1 μL. In this figure showed the behavior of the water droplet on the B-doped p-type Si (100) wafer with untreated condition to clarified the radical creation state. Fig. 2(a), (b) and (c) show the behavior of the water droplet on a wafer, only Ar gas with 10.0 L/min flow rate and the mixture of Ar and O_2 gas, respectively for 10 min treatment time were used with no plasma treatment. We have found that the surface treatment with low-pressure high-frequency plasma CVD to Si wafer will make the contact angle decrease from 35.8, 8.30 and 5.96 degree after the following condition. The O_2 gas flow rate in plasma CVD system caused the angle of water droplet decreased by using contact angle meter, and the observation of changing of radical in activated Si wafer surface. The radical formation on plasma process was considered to affect relationship of the changing in the contact angle by reforming at the wafer surface. The hydrophilic properties appeared on Si wafer surface when change gas in plasma process, the OH radical and the electrons incurred different of hydrophilic properties after surface treatment by improved the surface of Si wafer.

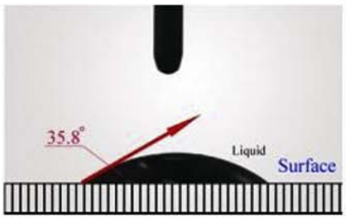
Fig. 3 shown the C1s high-resolution spectrum obtain by the narrow scanning spectrum method when measured by XPS after

Fig. 1. The system of low-pressure high-frequency plasma CVD system and photograph during plasma deposition.

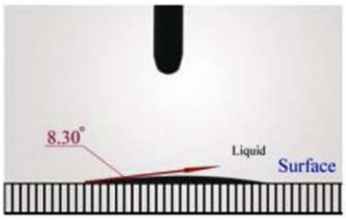
Table 1
Typical surface treatment by plasma CVD system.

Parameters	Condition
Ar flow rate	10 L/min
O_2 flow rate	0.1–0.6 L/min
RF-power	300 W
Treatment time	10 min

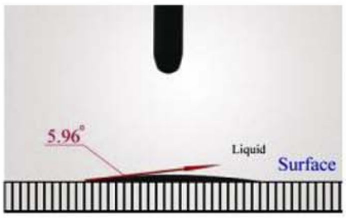
plasma surface treatment with Ar 10.0 L/min flow rate and the mixture of Ar gas 10 L/min flow rate and O_2 gas 0.3 L/min flow rate for 10 min by low-pressure high-frequency plasma chemical vapor deposition method. The difference of spectrum C1s when compared between Ar gas and the mixture of Ar and O_2 gas, and the investigation of spectra C1s in Ar gas not found O atom bonding. The spectrum of C1s from the mixture of Ar and O_2 gas in this figure were decomposed into 3 component peaks by curve-fitting using a Gaussian-type distribution. The component of C1s are C–H, C–O and O–C═O chemical bonding with about 286 eV, 287 eV and 290 eV binding energy, respectively [19–21]. We could clearly confirm that C–H, C–O and O–C═O bonding from this figure. The component ratio (percentage) of C1s in the mixture of Ar and O_2 gas on the surface were calculated from integral by C–H, C–O and O–C═O bounding are about 44%, 36% and 20%, respectively.



(a) No plasma surface treatment



(b) Surface treatment with Ar gas only



(c) Surface treatment with Ar+O_2 gas mixture

Fig. 2. Photograph of water droplet on Si wafers.

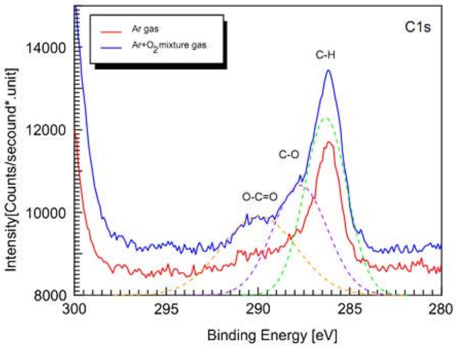


Fig. 3. XPS C1s scan spectra of Si wafer surfaces.

The radical production shown in Table 2, list of chemical reaction by considering relative experiment conditions of plasma CVD [22,23]. When Oxygen gas was added in low-pressure high-frequency plasma CVD system on the mixture of Ar and O_2 gas, the Oxygen could be dissociated by reaction (1) in Table 2. The major change which has seen in these comparisons suggests that Oxygen molecules bonding state on the wafer surface, and the radical Oxygen adheres on the wafer surface, while the chemical bonds on the wafer surface are maintained.

Fig. 4 shown the O1s high-resolution spectrum obtained by the narrow scanning spectrum method when measured by XPS under the same experimental conditions as in Fig. 3. The difference of spectrum O1s when compared only Ar gas and mixture of Ar and O_2 gas, we observed spectra O1s in Ar gas only and the mixture of Ar and O_2 gas found O1s increase more than on gas mixture condition with compare spectra in this figure. We could confirm that the difference in the spectrum O1s with about 533.5 eV binding energy with both Ar gas only and mixture of Ar and O_2 gas, it found spectra in this figure. When mixed O_2 gas in plasma, radical formation will increase, this happen due to the influence of electron and radicals on plasma [24].

Fig. 5 shown phenomenon and relationship of low-pressure high-frequency plasma CVD process. When oxygen were add in plasma gas with Ar + O_2 mixture gas, O_2 can be dissociated by chemical reaction (2), (3) and (4) in Table 2. From the O_2 dissociated by electron and O_2 gas from this reaction made the O radical increase. This means that radical oxygen and oxygen molecule are clearly generated in the plasma, and this is one index to confirm that radical reaction is definitely occured between the gas and wafer surface with low-pressure high-frequency plasma CVD.

Table 2
List of chemical reaction.

Chemical reaction	No.
$Ar + O_2 + e \rightarrow Ar^* + O + O^*$	(1)
$e + O_2 \rightarrow e + O + O$	(2)
$e + O_2 \rightarrow e + O + O(^1D)$	(3)
$O(^1D) + O_2 \rightarrow O + O_2$	(4)

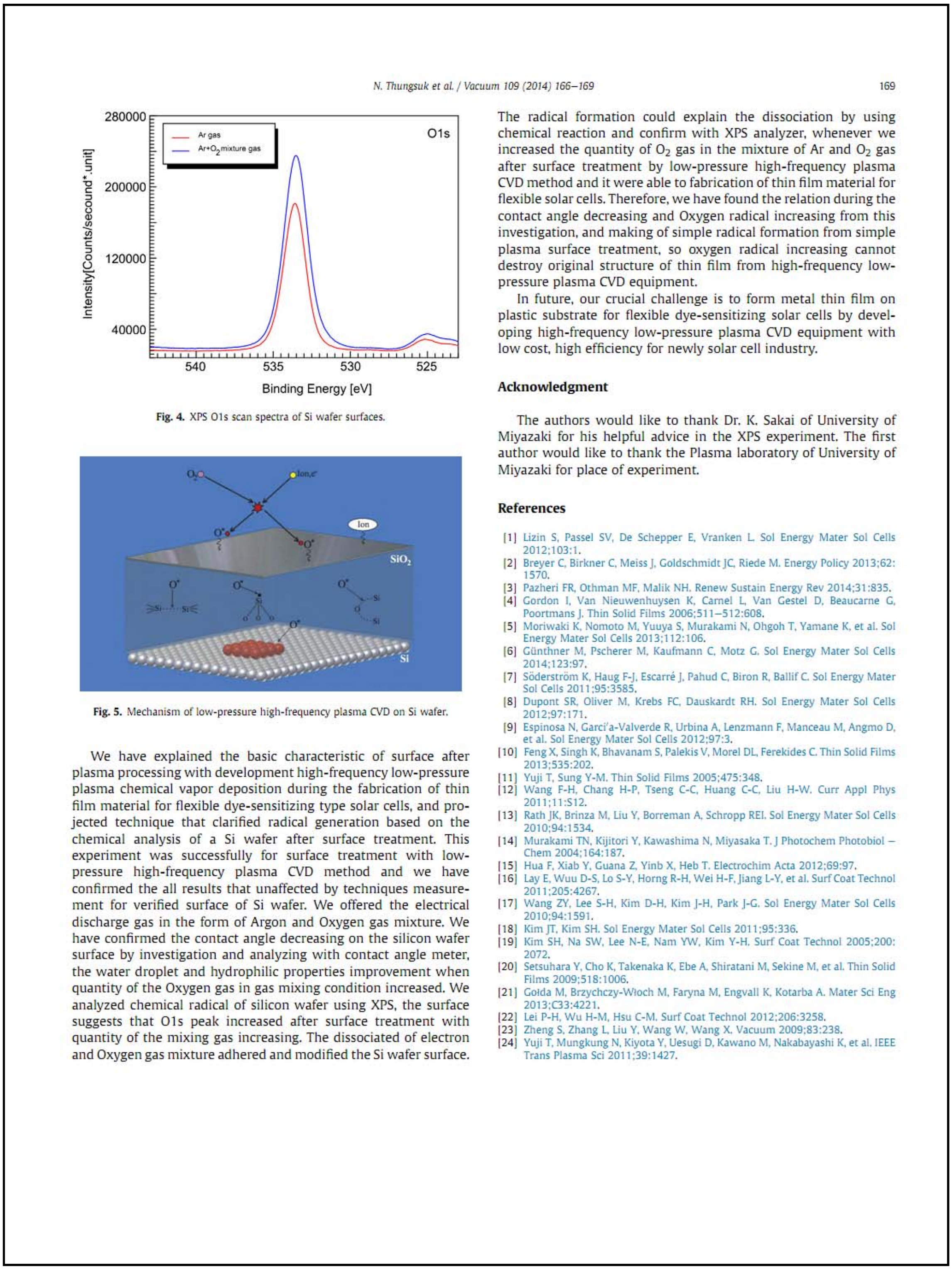


Fig. 4. XPS O1s scan spectra of Si wafer surfaces.

Fig. 5. Mechanism of low-pressure high-frequency plasma CVD on Si wafer.

We have explained the basic characteristic of surface after plasma processing with development high-frequency low-pressure plasma chemical vapor deposition during the fabrication of thin film material for flexible dye-sensitizing type solar cells, and projected technique that clarified radical generation based on the chemical analysis of a Si wafer after surface treatment. This experiment was successfully for surface treatment with low-pressure high-frequency plasma CVD method and we have confirmed the all results that unaffected by techniques measurement for verified surface of Si wafer. We offered the electrical discharge gas in the form of Argon and Oxygen gas mixture. We have confirmed the contact angle decreasing on the silicon wafer surface by investigation and analyzing with contact angle meter, the water droplet and hydrophilic properties improvement when quantity of the Oxygen gas in gas mixing condition increased. We analyzed chemical radical of silicon wafer using XPS, the surface suggests that O1s peak increased after surface treatment with quantity of the mixing gas increasing. The dissociated of electron and Oxygen gas mixture adhered and modified the Si wafer surface.

The radical formation could explain the dissociation by using chemical reaction and confirm with XPS analyzer, whenever we increased the quantity of O_2 gas in the mixture of Ar and O_2 gas after surface treatment by low-pressure high-frequency plasma CVD method and it were able to fabrication of thin film material for flexible solar cells. Therefore, we have found the relation during the contact angle decreasing and Oxygen radical increasing from this investigation, and making of simple radical formation from simple plasma surface treatment, so oxygen radical increasing cannot destroy original structure of thin film from high-frequency low-pressure plasma CVD equipment.

In future, our crucial challenge is to form metal thin film on plastic substrate for flexible dye-sensitizing solar cells by developing high-frequency low-pressure plasma CVD equipment with low cost, high efficiency for newly solar cell industry.

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References

[1] Lizin S, Passel SV, De Schepper E, Vranken L. Sol Energy Mater Sol Cells 2012;103:1.
[2] Breyer C, Birkner C, Meiss J, Goldschmidt JC, Riede M. Energy Policy 2013;62:1570.
[3] Pazheri FR, Othman MF, Malik NH. Renew Sustain Energy Rev 2014;31:835.
[4] Gordon I, Van Nieuwenhuysen K, Carnel L, Van Gestel D, Beaucarne G, Poortmans J. Thin Solid Films 2006;511–512:608.
[5] Moriwaki K, Nomoto M, Yuuya S, Murakami N, Ohgoh T, Yamane K, et al. Sol Energy Mater Sol Cells 2013;112:106.
[6] Günthner M, Pscherer M, Kaufmann C, Motz G. Sol Energy Mater Sol Cells 2014;123:97.
[7] Söderström K, Haug F-J, Escarré J, Pahud C, Biron R, Ballif C. Sol Energy Mater Sol Cells 2011;95:3585.
[8] Dupont SR, Oliver M, Krebs FC, Dauskardt RH. Sol Energy Mater Sol Cells 2012;97:171.
[9] Espinosa N, Garci'a-Valverde R, Urbina A, Lenzmann F, Manceau M, Angmo D, et al. Sol Energy Mater Sol Cells 2012;97:3.
[10] Feng X, Singh K, Bhavanam S, Palekis V, Morel DL, Ferekides C. Thin Solid Films 2013;535:202.
[11] Yuji T, Sung Y-M. Thin Solid Films 2005;475:348.
[12] Wang F-H, Chang H-P, Tseng C-C, Huang C-C, Liu H-W. Curr Appl Phys 2011;11:S12.
[13] Rath JK, Brinza M, Liu Y, Borreman A, Schropp REI. Sol Energy Mater Sol Cells 2010;94:1534.
[14] Murakami TN, Kijitori Y, Kawashima N, Miyasaka T. J Photochem Photobiol – Chem 2004;164:187.
[15] Hua F, Xiab Y, Guana Z, Yinb X, Heb T. Electrochim Acta 2012;69:97.
[16] Lay E, Wuu D-S, Lo S-Y, Horng R-H, Wei H-F, Jiang L-Y, et al. Surf Coat Technol 2011;205:4267.
[17] Wang ZY, Lee S-H, Kim D-H, Kim J-H, Park J-G. Sol Energy Mater Sol Cells 2010;94:1591.
[18] Kim JT, Kim SH. Sol Energy Mater Sol Cells 2011;95:336.
[19] Kim SH, Na SW, Lee N-E, Nam YW, Kim Y-H. Surf Coat Technol 2005;200:2072.
[20] Setsuhara Y, Cho K, Takenaka K, Ebe A, Shiratani M, Sekine M, et al. Thin Solid Films 2009;518:1006.
[21] Gołda M, Brzychczy-Włoch M, Faryna M, Engvall K, Kotarba A. Mater Sci Eng 2013;C33:4221.
[22] Lei P-H, Wu H-M, Hsu C-M. Surf Coat Technol 2012;206:3258.
[23] Zheng S, Zhang L, Liu Y, Wang W, Wang X. Vacuum 2009;83:238.
[24] Yuji T, Mungkung N, Kiyota Y, Uesugi D, Kawano M, Nakabayashi K, et al. IEEE Trans Plasma Sci 2011;39:1427.