J Electr Eng Technol.2015;10(1): 295-298
http://dx.doi.org/10.5370/JEET.2015.10.1.295

ISSN(Print) 1975-0102
ISSN(Online) 2093-7423

Fabrication of Ozone Bubble Cleaning System and its Application to Clean Silicon Wafers of a Solar Cell

J. K. Yoon* and Sang Heon Lee†

Abstract – Ozone micro-bubble cleaning system was designed, and made to develop a unique technique to clean wafers by using ozone micro-bubbles. The ozone micro-bubble cleaning system consisted of loading, cleaning, rinsing, drying and un-loading zones, respectively. In case of the cleaning the silicon wafers of a solar cell, more than 99 % of cleaning efficiency was obtained by dipping the wafers at 10 ppm of ozone for 10 minutes. Both of long cleaning time and high ozone concentration in the wet-solution with ozone micro-bubbles reduced cleaning efficiency because of the re-sorption of debris. The cleaning technique by ozone micro-bubbles can be also applied to various wafers for an ingot and LED as an eco-friendly method.

Keywords: Ozone micro-bubble, Wafer, Wet-solution, Eco-friendly method

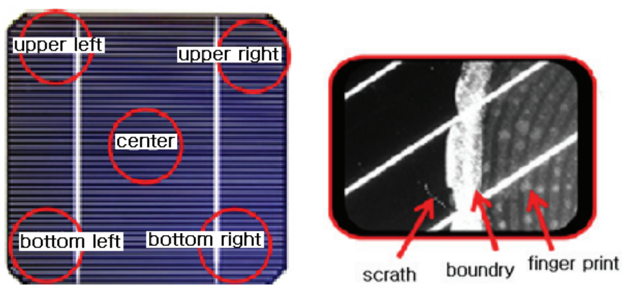
1. Introduction

Techniques to clean wafers during semi-conductor and solar cell fabrications are one of important processes to make a high quality products, especially, a high performance silicon solar cell [1]. There are various wet techniques to clean the wafers such as ionized water cleaning, ultrasonic cleaning, low pressure plasma and mechanical methods [2, 3]. Since the wet process, so called RCA process, uses acid and alkaline solutions with harmful chemicals, it has an environmental problems like waste disposal cost and environmental regulation due to a large amount of waste water [4]. Recently, a cleaning technique by ozone has been attractive attention as eco-friendly process without usage of harmful chemicals [5]. The ozone has so short half-life so to clean effectively organic debris and metal dust on a wafer. The washing and cleaning mechanisms by the ozone were relatively well established in chemistry. The ozone was self-dissociated in air and water, which dissociation rate depends on pH, concentration, temperature and pressure. There are two reaction routes for the ozone to react organic molecules. One is a direct reaction by a dissolved ozone and the other is an indirect reaction by a hydroxyl radical. The direct reaction usually occurs in an acid solution because a met-stable phase by the reaction between an organic molecules and ozone is formed and its transformation rate to be final phases like oxides is quite slow [6]. This kind properties of the reactions can be used for the ozonation technology to remove various contaminated organic compounds on a wafer. The ozonated water used to wash a silicon wafer of a solar cell has so strong oxidizing powder as to make a thin silicon oxide film on the wafer surface with the reaction of $Si + 2O_2 \rightarrow SiO_2 + 2O_2$. In order to apply the ozonation technology as an economic process, an industrial applicable ozone generator should be designed, with which an optimum condition should be selected to retard an evaporation of ozone in air, control a fast self-dissociated reaction of ozone in a water by carbon dioxide gas. Hence the objectives of this study are to design and make an ozone-generation system, to develop an eco-friendly cleaning process to replace a commercial wet clean process using acid and alkine agents, and characterize its properties to clean wafers during a solar cell fabrication in industry.

† Corresponding Author: Dept. of Electronic Engineering, Sunmoon University, Korea. (shlee1152@hanmail.net)
* SFC Co., LTD, Korea. (yjktop@korea.com)
Received: October 10, 2013; Accepted: February 6, 2014

2. Experimental Method

An ozone-generation system to produce micro-bubbles was designed and domestically fabricated to apply to a wafer for a silicon solar cell. Main parameters of the system to make ozone were oxygen flux, voltage, frequency. Amount of generated ozone was determined by measuring the exothermic heat of a quartz per hour, amount of oxygen gas formation and applied voltage. Artificial surface



(a) (b)

Fig.1. Five positions of a finger printing method to determine cleaning efficiency: (a) five point; (b) boundary of natural and artificial contaminations

contamination was used by spraying inorganic fine particles. Five pont-finger printing marked by a oil pen was used for artificial organic contamination on the wafer surface. They were washing and cleaned by the ozone micro-bubble cleaning system for the microscopic observation. Optimum cleaning efficiency was determined by observing a contaminated surface with a polarization microscope (Foculus, IMB-15FT,Germany) and scanning electron microscope (Hitachi S-4300, Japan), respectively. Fig. 1 is five positions of the finger printing method to study cleaning efficiency.

3. Results and Discussion

3.1 Fabrication of an ozone micro-bubble cleaning system

In this study, an ozone-generation system to make micro-bubbles for cleaning silicon wafers was designed and fabricated. The cleaning system consisted of loading, cleaning, rinsing, drying and un-loading zones, respectively. The drying zone had two modules like a hot distilled water and an air blower to improve dry efficiency. Fig. 2 and 3 are schematic diagrams of ozone micro-bubble cleaning system and an ozone generator, respectively. Fig. 4 and 5 are photos of an ozone generator and an ozone mixing tank, respectively. The ozone gas formed by the ozone generator goes to a wafer cleaning bath through the ozone mixing tank. Each regulator-solenoid valve-oxygen generator-ozone generator unit was modulated to find the maximum production of ozone. Amount of ozone gas into an inlet pump is related to the amount of generated ozone gas and pump pressure, which is expressed by the following

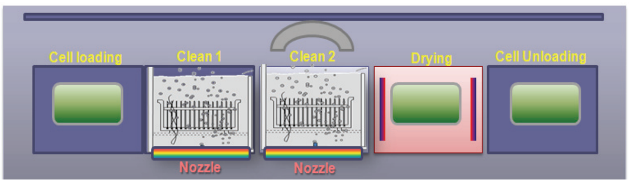


Fig. 2. Schematic diagram of ozone micro-bubble cleaning system

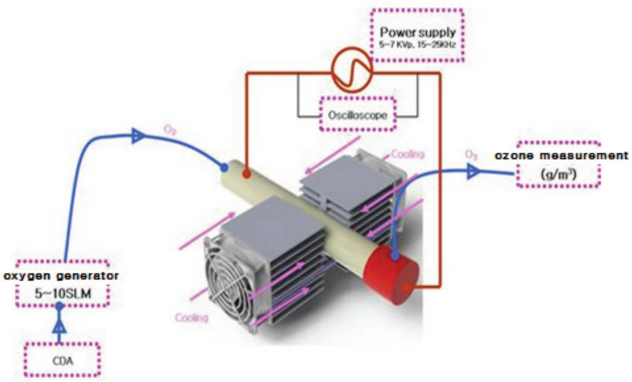


Fig. 3. Schematic diagram of an ozone generator

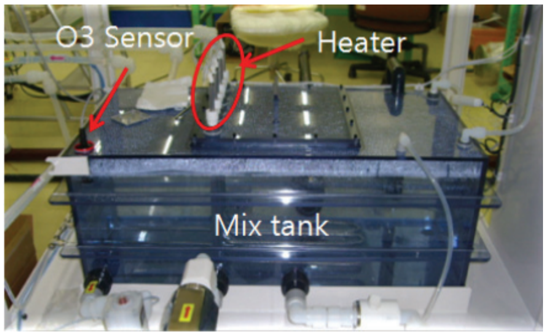


Fig. 4. Photo of an ozone mixing tank

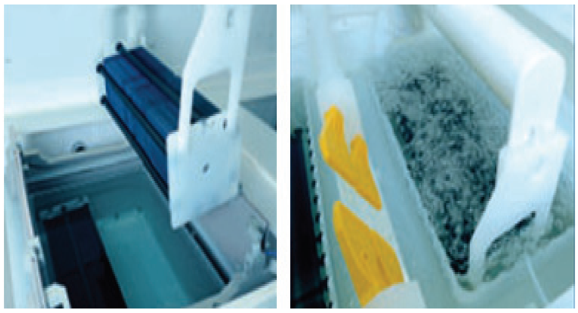


Fig. 5. Photo of an ozone mixing tank

equation:

$$\text{Amount of ozone} = \text{Constant} \times \text{ozone concentration} \times \text{oxygen flux} \quad (1)$$

Micro-bubbles can be produced by mixing a liquid formed by a bubble jet and a gas through a nozzle with a pumping pressure. The liquid and gas phases are usually distilled water and air, respectively. Since high pressurized nano-sized and micro-bubbles reach on a surface, they can physically remove dusts on a wafer surface. There are three types of micro-bubble generation methods like using filter, pressure and micro-bubble jet. Among these methods, the micro-bubble jet method is changeable to mass-produce ozone micro-bubbles in industry because of simple replacement of the ozone to oxygen gases. The oxygen micro-bubble generator made in this study showd the maximum efficiency at the regulator pressure of 0.2~0.3 MPa, oxygen outlet flux of 0.6~1.2 kgf/cm^2, and oxygen outlet flow of 0.3~1.0 LPM, respectively. A sensor controlled by a transfer robot was attached in a after loading unit for well installation of the wafer. Nozzle angle of the hot dry unit was optimized by changing the angle in the ranges of 90~120°, which was analyzed by using Solidworks Flow Simulation Program working Window XP Professional X64 Edition with Intel Core2 Qual CPU.

3.2 Characterization of ozone micro-bubble cleaning

Table 1 is operating parameters of the ozone micro-bubble cleaning system which was designed and fabricated in study. Fig. 6 is cleaning rate and time of the ozone

Table 1. Operating parameters of the ozone micro-bubble cleaning system

parameters	operating range
pump pressure [MPa]	0.02 ~ 0.04
air inlet [LPM]	2.5 ~ 3.8
temperature [℃]	35 ~ 38
dipping time [minute]	10 ~ 15
ozone concentration [ppm]	10 ~ 15
contaminated materials	organic and inorganic debris

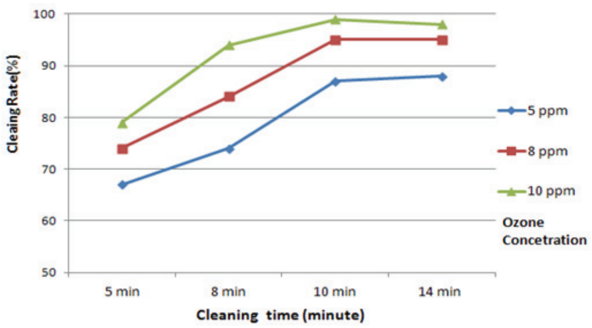


Fig. 6. Photo of an ozone mixing tank

micro-bubble cleaning system with ozone concentration in a washing solution. The cleaning rate was determined by measuring a removed contamination area which was marked by an oil pen. As shown in Fig. 6, it is clear that 10 minutes cleaning with 10 ppm of ozone concentration is the most effective in this test condition. In oder to compare cleaning efficiencies of the ozone micro-bubble method to the conventional oxygen micro-bubble method and the ozone bubble with distilled water method, artificial contaminations like finger-printing and fine silica particles were applied to silicon wafers after texturing process. The contaminated wafers were dipped and washed by each method at 38℃ for 12 minutes in 10 ppm of ozone concentration, respectively, and finally analyzed by optical microscopy. Fig. 7 is the cleaning rate with cleaning methods. As shown in Fig. 7, the cleaning rate was in the order of ozone micro-bubble method with more than 95 %, conventional oxygen micro-bubbling with about 84 %, and ozone-bubble with distilled water of about 76 %, respectively. It is interesting why the ozone micro-bubble method is effective to cleaning organic and inorganic contaminations. The ozone in an aqueous solution is known to become OH-radical which reacts with organic molecules. After removal of the organic contamination on a surface, new oxide layer with hydrophilic property is formed on the surface of the silicon wafer [7]. It means that the hydrophilic property of the surface is one of important fact for cleaning efficiency of the organic contamination. In this study, contact angle of the washing solution was determined. Fig. 8 is the contact angle variation of a washing droplet on a silicon wafer by an ozone micro-bubble cleaning method. As shown in Fig. 8, the as-received wafer surface has 40.8° contact angle, which reduced less than 20° after ozone micro-bubble cleaning. It supports that the

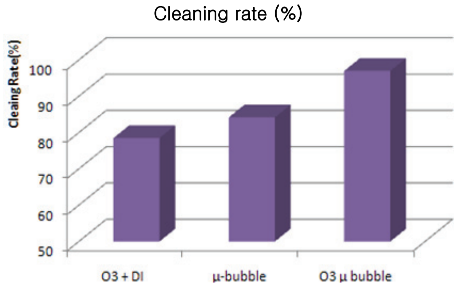


Fig. 7. Cleaning rate with cleaning methods

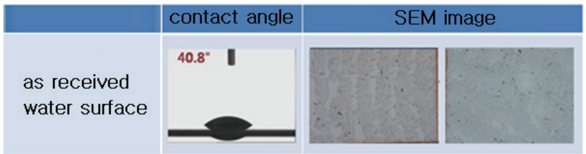


Fig. 8. Contact angle variation of a washing droplet on a silicon wafer by an ozone micro-bubble cleaning method

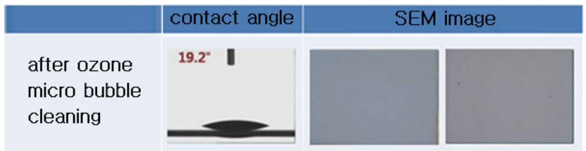


Fig. 9. Contact angle variation of a washing droplet on a silicon wafer by an ozone micro-bubble cleaning method

silicon wafer surface changed from hydrophilic to hydrophobic properties by the ozone micro-bubble cleaning. Fig. 9 is scanning electron micrographs of silicon wafer surface of a solar cell after texturing step during the solar cell fabrication process. The texturing step was carried out after ozone micro-bubble cleaning at 10 ppm of the ozone concentration for 10 minutes. The texturing condition was at 75℃ for 30 minutes in KOH / IPA solution. As shown in Fig. 9, relatively uniform surface with about 61°±2° textured angles was well formed, which uniformity was more than 98% in production scale. It means that the ozone micro-bubble cleaning is one of effective cleaning techniques which can be applied to various wafers such as solar cell, an ingot and LED.

4. Conclusions

In this study, ozone micro-bubble cleaning system for silicon wafers of a solar cell was developed and its characterization was systematically studied. For the cleaning of the wafers of the solar cel, more than 99 % cleaning efficiency was obtained by dipping the wafers at 10 ppm of ozone for 10 minutes. Both of long cleaning time and high ozone concentration in a wet-solution reduced cleaning efficiency because of the re-sorption of debris. The ozone micro-bubble cleaning method can be directly applied to wash silicon wafers of the solar cell and various wafers for an ingot and LED. The ozone micro-bubble cleaning method as an eco-friendly method is one of practically alternative methods to a conventional RCA method for reduction of harmful agents.

Acknowledgements

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIP) (Grant No.NRF-2013M2B2A4036157).

References

[1] W. Kern, Handbook of Semiconductor Wafer Cleaning Technology, Noyes Publication, 1993, p. 383-391.
[2] J Wei, S. Verhaverbeke, Cleaning Technology in Semiconductor Device Manufacturing, The Electrochemical Society, 1998, p. 496-504.
[3] S Nelson, Ozonated Water for Wafer Cleaning and Photoresist Removal Solid State Technology, 1999, p. 107-112.
[4] Lange's Handbook of Chemistry, 15th edition, McGraw Hill, Inc. New York. 1999.
[5] Rice Aharan Netzer, Handbook of Ozone Technology Vol. II, Ann Arbor Science Book, 1984.
[6] D. Bahnemann and Edwin J. Hart, "Rate constants of the reaction of the hydrated electron and hydroxyl radical with ozone in aqueous solution" J. Phys. Chem., Vol. 86, pp. 252-255, 1982.
[7] W. Kern, "The Evolution of Silicon Wafer Cleaning Technology" J. Electrochem. Soc., Vol. 137, no. 6, pp. 1887-1892, 1990.

Jong-Kuk Yoon was born in Daejon, Korea, in 1966. He received the B.S. degree from Department of Materials engineering, Chungnam National University in 1993 and he received Ph.D degree from Kyungpook National University. 2002. He was an IC Process engineer for Motorola Inc. USA. He was a senior researcher for Kolon Central Research Institute. He was a Principle researcher for Kumho Petrochemical research institute. Currently, He works for R&D Director for SFC research institute.

Sang-Heon Lee He received M.S degree in Department of Electronic Engineering from TOKAI University, Japan. He received Ph.D degree in Department of Electronic Engineering from TOKAI University, Japan. His research interests are fabrication technology for high Tc superconductors, magnetic materials, and physical properties. He is a Professor, Department of Electronic Engineering, Sunmoon University.