Feature Article

The Chemicals used in PV Manufacturing and its Monitoring
太陽電池製造工程で用いられる薬液とその計測

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Photovoltaic (PV) cells have been attracting the attention as the source of clean energy, and its market is drastically rising now. In its manufacturing processes, wet process is the key technology for it's quality and cost. In this paper, the main wet processes, the monitoring for them and the prospect of the wet process monitoring is described.

太陽電池は，近年クリーンエネルギー源として注目をされており市場は活況である。その製造工程において，ウェットプロセスは品質とコストを左右する重要な技術である。主に使用されているウェットプロセスと，そのモニタリングの特色および今後の展望について述べる。

Introduction

— Overview and Situation of Photovoltaic (PV) Cells —

Recent Photovoltaic (PV) system demand is drastically growing due to global warming, political measures in many countries and high oil prices, and the market is booming. The worldwide shipping of PV cells was 10 GWp as electrical energy in 2009, and according to one forecast, it will increase to up to 30 GWp in 2013, nearly 3 times than in 2009.[1] The growth of China is outstanding. It accounts for 35% of the total world PV cell production capacity in 2009, which is 6 times greater than in 2006. It got 1st prize. After China, follows EU (24%), Japan and North America[2]. One of the factors of the explosive increase is that the cost of electrical power generation by conventional methods and by PV is becoming comparable.

While this is caused in part by political encouragement such as Feed-in-Tariff, from an engineering point, high energy conversion efficiency and low price is the key factor. PV cell is separated into multiple categories according to its materials; silicon-based, compound semiconductor-based and organic- based cells. Furthermore, the silicon-based PV cell is categorized into crystalline-based and thin film-based cells. The mainstream today is Si crystalline-based PV, it accounts 70% of the overall production[3]. The Crystalline silicon cell manufacturing and semiconductor manufacturing share many of the same processing techniques, since they both use Si wafers, and it is often the case that semiconductor manufacturing equipment makers expand their field into the PV market HORIBA also supplies it's products to PV market, taking advantage of the know-how obtained from leading wet process monitoring in semiconductor manufacturing for over 20 years. In this paper, wet processes applied in the PV manufacturing and the current situation and the future prospect of chemical concentration monitoring is described.

Manufacturing Process of Crystalline Si PV

The structure of crystalline Si PV is that a p-n junction is formed on the surface of P doped Si wafer, then anti-reflection coating and grid electrodes are built on the

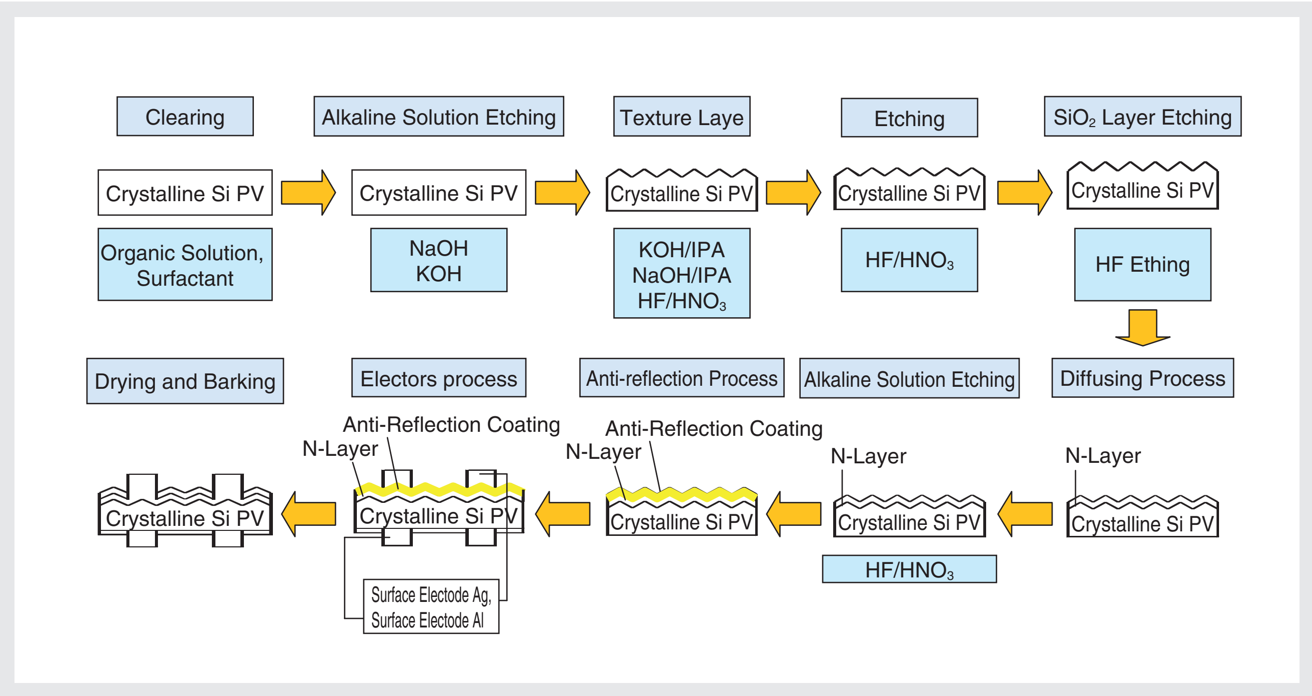


Figure 1 Schematic flow of manufacturing processes of PV cells and chemicals used at every step

n-layer. On the back side, the back surface electrode and electric field layer is built. Figure 1 Schematic flow of manufacturing processes of PV cells and chemicals used at every step Before processing the wafers, particles are removed by organic solution after slicing Si wafers. For the purpose to remove saw damage, alkaline solution etching is performed with NaOH or KOH. The most unique step of PV manufacturing is forming a "Texture layer" on the Si wafer in order to reduce the reflection loss from the surface. Generally, flat Si wafer reflects 1/3 of the incident light, and it is quite a large energy loss.[4] It is a widely applied technique to form textures on the surface in order to reduce reflection loss from the Si wafer surface and to improve energy efficiency.

In the case of monocrystalline silicon, pyramid-patterned structures are formed on the surface by anisotropic etching with an alkaline solution. This process takes advantage of the nature of Si crystal that when it is etched with alkaline, etching speed of (111) surface of Si crystal is more rapid than (100) surface, so the (111) surface remains and a pyramid shaped surface is formed. Generally, KOH / IPA mixture is used for this process, in some cases, NaOH is used instead of KOH as NaOH costs less than KOH. Si etching by alkaline process is expressed by the chemical reaction (1) shown below.[5]

$$Si + 2H_2O + 2OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2\uparrow \quad \cdots\cdots\cdots\cdots (1)$$

On the other hand, since the crystal orientation is not uniform in the polycrystalline silicon, it is not possible to pattern the uniform textures by alkaline etching like monocrystalline silicon. Therefore, a mask layer is formed on the wafer surface and the mask is removed by laser patterning and etc. And isotropic etching is performed with an HF / HNO_3 mixture, which forms hemispherical textures.[6] In this process, Si is oxidized by HNO_3 which is strong oxidant, and SiO_2 is dissolved by HF as the chemical reactions below.[7]

$$3Si + 4HNO_3 \rightarrow 3SiO_2 + 4NO + 2H_2O \quad \cdots\cdots\cdots\cdots (2)$$

$$SiO_2 + 6\,HF \rightarrow H_2SiF_6 + 2H_2O \quad \cdots\cdots\cdots\cdots (3)$$

With using HF solution, SiO_2 layer and particles generated as texture patterning are removed, then p-n junction is formed by diffusing phosphorus chemical. When n-layer is diffused on the wafer's rear and side surfaces, it causes problem such as leak current or short circuit. In order to prevent such problems, the diffused layer is removed by physically cutting the edge of the wafer or performing chemical etching with HF / HNO_3 mixture.[8] After forming p-n junction, anti-reflection layer is formed, electrical circuits are printed on the front rear surfaces, through drying and baking processes, then PV cells are completed. As shown above, various chemicals are used in the etching and cleaning processes of general PV manufacturing processes.

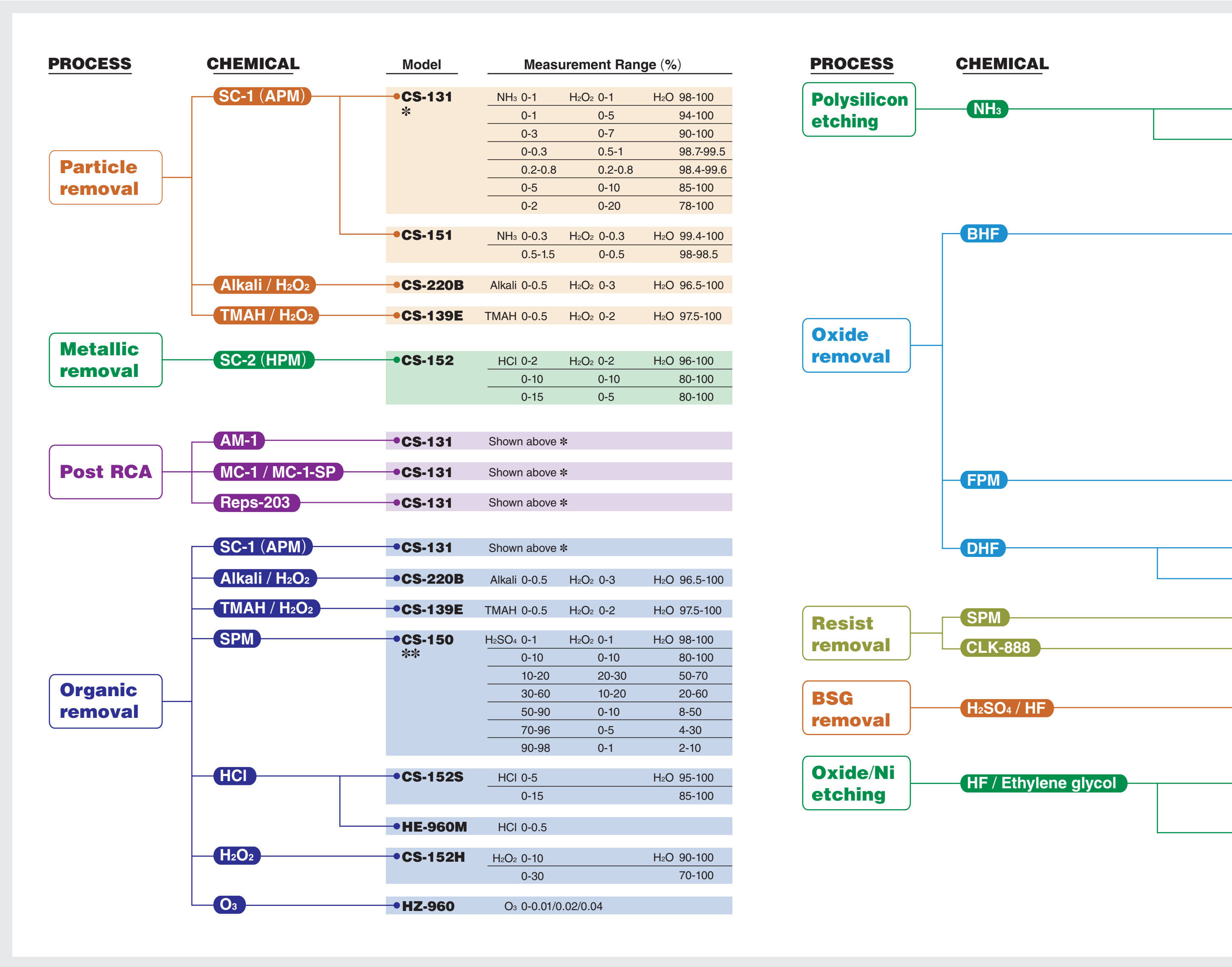


Figure 2 CS series lineup of various monitors

Features of Chemical Concentration Monitors in PV Manufacturing Processes

Though monitoring concentration of chemical solution has been recognized as necessary technology for controlling quality in semiconductor manufacturing processes, in PV manufacturing, it is not regarded the same as in the semiconductor industry. Recently, the importance of concentration monitoring is gradually realized as the key for not just managing product quality but saving cost and lowering environmental-load by reducing the chemicals used in wet processes. In some cases, chemical concentration monitoring is used not just to monitor the concentration but also for feed-back control.

Under such situations, the major difference between monitoring for PV and semiconductor processes is shown blow.

1) Stable monitoring under the coexistence of by-product...
   It is often the case in PV manufacturing processes that the chemical is used for a long time without chemical change. It is necessary to monitor chemical concentration precisely in the presence of by-products, and to monitor the concentration of the by-products for chemical lifetime control.
2) Ability to monitor low temperature and high temperature sample. Many processes are under the condition that acids are low chemical temperature (5-10 deg.C) and alkalis are high (70-90 deg.C).

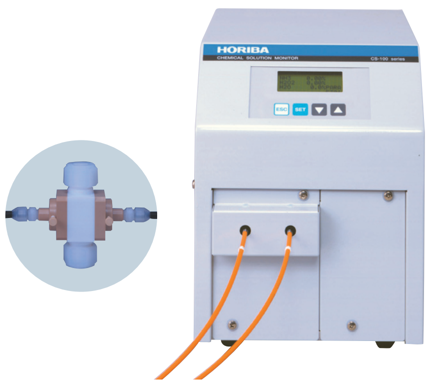
Model	Measurement Range (%)		
HF-960M	NH_3 0-0.5		
CS-131S	NH_3 0-0.2		H_2O 99.8-100
	0-1		99-100
	0-5		95-100
	0-29		71-100
CS-137	NH_4F 0-10	HF 0-3	H_2O 87-100
	4-5	0.5-1.5	93.5-95.5
	15-21	0-3	76-85
	15-25	0-3	72-85
	16-18	0-0.5	81.5-84
	19-21	4-6	73-77
	19-21	5-8	71-76
	25-30	0-1	69-75
	29-31	5-7	62-66
	32-34	3-5	61-65
	35-38	3-5	57-62
	37-39	1-3	58-62
	39-40	0-0.5	59.5-61
CS-153	HF 0-0.5	H_2O_2 0-9	H_2O 90.5-100
	0-1.5	0-1	97.5-100
	0-10	0-10	80-100
CM-210	HF 0-1/2/5/10/20/50		
HF-960M	HF 0-0.5		
CS-150	Shown on the left **		
CS-139K	ALKAL 0.5-2	H_2O_2 1-5	Others 93-99
CS-133V	H_2SO_4 83-93	HF 0-5	H_2O 2-17
	80-96	1-5	4-19
	HF 0.5-1.5	H_2O 2-4.5	H_2SO_4 94-98
CS-138	HF 0-5	H_2O 0-10	EG 85-100
	5-10	7-12	78-88
CS-138W	HF 0-5	EG 85-100	H_2O 0-10
	0-5	0-10	85-100

PROCESS	CHEMICAL	Model	Measurement Range (%)		
Al etching	HNO_3 / CH_3COOH / H_3PO_4	CS-139J	HNO_3 0-5	CH_3COOH 0-3	H_3PO_4 65-75
			1-3	8-12	70-75
			1.5-5.5	9-11	65-75
			4-6	8-10	65-70
			4-7	7.5-10.5	69-75
			8-13	8-13	60-65
Polymer removal	HNO_3 / HF	CS-153N	HNO_3 60-70	HF 0-5	H_2O 25-45
			50-60	5-10	30-45
			57-65	3-8	27-40
			69-70	0-0.5	29.5-31
			68.5-70	0-1	29-31
	H_2O / Amine	CS-135B	H_2O 26-50	A.B.F 3-10	AMINE 45-71
	H_2O / Other	CS-135D	H_2O 10-30	Others 70-90	
	EF-1	CS-135E	HF 0-0.2	H_3PO_4 0.2-5	Others 94.8-99.8
	ALKALI	CS-139R	ALKAL 2-3	H_2O_2 0-3	Others 94-98
Low-K etching	LK-1	CS-135A	H_2O 90-100	XXX 0-10	
Others	HNO_3 / HCl	CS-152N	HNO_3 5-12	HCl 15-25	H_2O 63-80
			8-10	17-21	69-75
PV	NaOH / Na_2SiO_3		NaOH 8-14	Na_2SiO_3 0-10	H_2O 76-92
	NaOH / IPA / Na_2SiO_3		NaOH 0-7	IPA 0-7	Na_2SiO_3 0-7
	KOH / K_2SiO_3		KOH 0-10	K_2SiO_3 0-10	H_2O 80-100
	KOH / IPA / K_2SiO_3		KOH 0-3	IPA 2-5	K_2SiO_3 0-10
	HF / H_2SiF_6		HF 0-10	H_2SiF_6 0-2	H_2O 88-100
	HNO_3 / HF / H_2SiF_6		HNO_3 20-35	HF 5-12	H_2SiF_6 0-20
			20-35	5-27	0-20
			28-48	2-15	0-25
			37-48	7-17	0-10
			30-60	0-7	0-15
			30-60	0-10	0-15
			50-67	1-7	0-10
	HNO_3/HF/CH_3COOH		HNO_3 20-40	HF 0-1	CH_3COOH 8-12

CS Series – Monitor for Multi Component Chemicals

To meet such demands, HORIBA has a lineup of various monitors as shown in Figure 2. In such monitors, the CS-100 series is the one for multi component chemicals including by-product[9] CS-100 series applies UV and NIR absorbance spectroscopy. The spectrum in NIR area, various high-mode vibration and hybrid oscillations are intricately overlapped[10] and samples rarely obey Lambert-beer's law, as absorbance increases in proportion to it's concentration. Moreover, in UV areas, there exists various absorbance of molecules and ions, and every components' absorbance spectrums overlap. In order to calculate the concentration of each components from such complex spectrums, multivariate statistical analysis is applied. For calculating the concentration of multiple chemicals rapidly, it is necessary to detect the absorbance at many wavelengths -which is in other words absorbance spectrums- CS-100 series realizes high-speed detection with HORIBA's originally developed spectrometer with multi-channel detector. Measurement interval of CS-100 series is approximately 3 seconds for standard type, 0.5 seconds for high speed type. When monitoring high or low temperature chemicals, heat exchanger can be provided as optional unit to heat or cool the sample to near room temperature. In case little space is allowed at the sampling point or monitoring high temperature chemical directly, a fiber type monitor- CS-100F1 is suitable. With this design, sampling cell is separated from the monitor main unit's electrical and optical components.[11] Besides performance, the CS-100 series are highly regarded since they are simple to set up without complicated calibrations, and require no periodical calibration other than background correction by DIW performed once in 6months. Figure 2 Chemical concentration monitor CS-100 / 100F1 series. CS-100 series is available for more than 100 chemical solutions. One of the examples shown in Figure 5 is the continuous measurement stability data of KOH / IPA monitor. (Sample : KOH : 1.5 mass%, IPA : 3.0 mass%, Measurement interval 3sec)

CS-100 Series



CS-100 Series (Optical Fiber Type)

Figure 3 Chemical concentration monitor CS-100 / 100F series

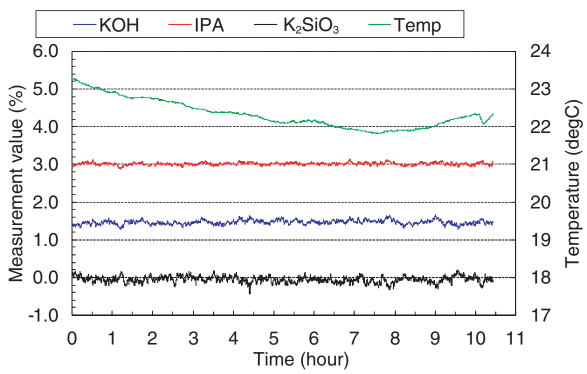


Figure 4 Continuous measurement stability result of KOH / IPA monitor

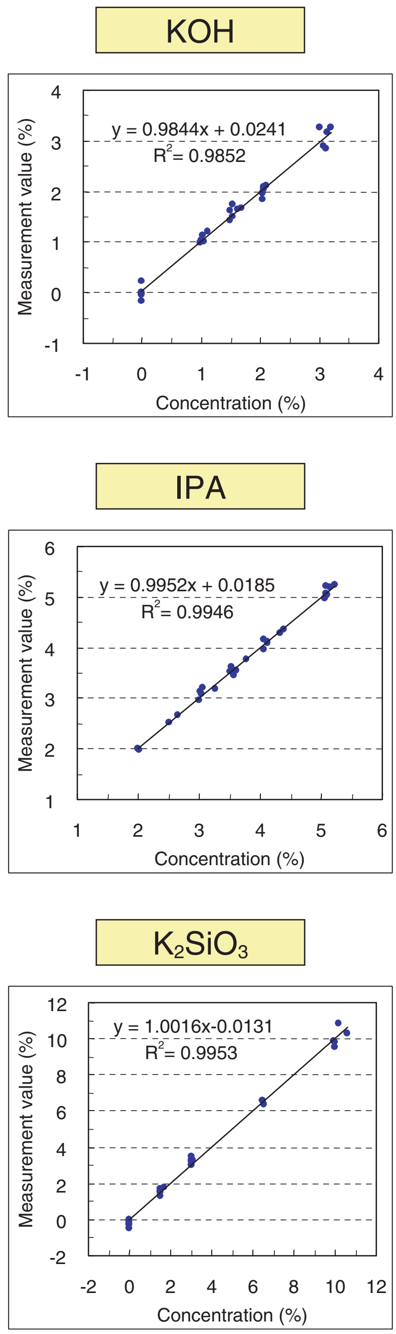


Figure 5 Linearity performance of CS-100 KOH/IPA solution monitor

Conclusion

— Expectation of the Chemical Concentration Monitor in the PV Market —

Backed by technical progress and fierce cost competition, it is expected that more accurate monitoring of by-products will be needed for more and more high quality product and high throughput.
Also, monitoring of original chemicals or compositions for particular PV makers will be needed.
Our mission is to deliver solutions for customers' requests for the new ideas and problems, contribute to their production efficiency, and moreover to contribute to improve technology for PV as a clean energy source.

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