Low-cost Contact Formation of High-Efficiency Crystalline Silicon Solar Cells by Plating

D. S. Kim, E. J. Lee, J. Kim and S. H. Lee*

Abstract High-efficiency silicon solar cells have potential applications on mobile electronics and electrical vehicles. The fabrication processes of the high efficiency cells necessitate complicated fabrication processes and expensive materials. Ti/Pd/Ag metal contact has been used only for limited area in spite of good stability and low contact resistance because of its expensive material cost and processes. Screen printed contact formed by Ag paste causes a low fill factor and a high shading loss of commercial solar cells because of high contact resistance and a low aspect ratio. Low cost Ni/Cu metal contact has been formed by using a low cost electroless and electroplating. Nickel silicide formation at the interface enhances stability and reduces the contact resistance resulting in an energy conversion efficiency of 20.2% on 0.5 Ωcm FZ wafer. Tapered contact structure has been applied to large area solar cells with 6.7 x 6.7cm^2 in order to reduce power losses by the front contact. The tapered front metal contact is easily formed by the electroplating technique producing 45 cm^2 solar cells with an efficiency of 21.4% on 2 Ωcm FZ wafer.

Key words Solar cell, Contact, Plating, Nickel, Copper

* Strategic Energy Research Institute, Electronics Engineering, Sejong University
■ 98 Gunja-dong, Gwangjin-ku, Seoul, Korea 143-747
■ E-mail : shl@sejong.ac.kr ■ Tel : (02)3726-3725 ■ Fax : (02)3408-3329

1. INTRODUCTION

PV market of crystalline silicon solar cells has been increased from 67.9% in 1990 to 95.6% in 2003. The efficiency of crystalline silicon solar cells has been greatly improved over the last few years. With conversion efficiency over 24% (1), the efficiency of silicon solar cell is approaching theoretical limit of silicon homo-junction. However, the production of crystalline silicon solar cells with such high efficiency is very small compared to that of conventional silicon solar cells because of complicated fabrication processes with cost intensive process steps and small area. It is expected that production of single crystal silicon modules will reach efficiency of 22% by 2010 (2). In order to commercialize high efficiency solar cells, it is important that the fabrication process should be cost effective without sacrificing the performance. The number of photolithography processes can be reduced to only one step to achieve efficiency of over 20%. Evaporated Ti/Pd/Ag contact has been widely used for high efficiency cells. However, the evaporation process is not applicable to mass production because high vacuum is needed. Furthermore, those metals are too expensive to be applied for terrestrial applications. Copper is promising material for the electrical contact of solar cells in terms of conductivity and cost. Ni monosilicide (NiSi) has been proposed as a suitable silicide for the salicidation process and expected to replace conventional silicides, $TiSi_2$ and $CoSi_2$ due to its low resistivity, low formation temperature (350-750℃), low film stress. Furthermore, Ni is known to be a suitable diffusion barrier to Cu. The resistivity of NiSi thin films has been reported to be 14 $\mu\Omega$cm which is comparable to that of $TiSi_2$ (13-16 $\mu\Omega$cm) (3,4). In the case of nickel silicidation during rapid thermal annealing, Ni film is converted progressively to Ni_2Si (200-300℃), NiSi (300-700℃), and $NiSi_2$ (700-900 ℃) with increasing annealing temperature.

As solar cell size is increased, the ohmic loss due to the grid finger becomes dominating factors to affect cell performance. Cross sectional area of the front grid finger needs to be increased as the solar cell size increases since the current density through the grid finger increases. On large area solar cells, therefore, compromise between the shading loss and the resistive losses due to the front grid is need. The front contact formation by plating can provide high fill factor on large area solar cells without sacrificing the current density significantly.

In this study, we report the contact formation process and mechanism of Ni/Cu system and how to achieve high fill factor on large area solar cells.

2. EXPERIMENTAL

P-type, (100), 0.5 – 2 Ωcm, 500 μm thick float zone (FZ) silicon wafers were used to fabricate high efficiency silicon solar cells. Inverted pyramids were formed on the front surface by photolithography process and KOH etching to reduce front surface reflectance. Heavy phosphorus diffusion was performed selectively where the front metal contact was to be formed. Lighter emitter with sheet resistance of 150 $\Omega/\square$ was formed on active area by phosphorus diffusion after the heavy diffusion. Rear contact holes of 200 μm diameter on a 2 mm × 2 mm matrices were generated by photolithography process. Standard metal contact was formed by Ti/Pd/Ag evaporation on the front and rear sides followed by Ag electroplating to compare with the new contact system. The front of cells were passivated by silicon dioxide in Trans-LC and oxygen at 1050℃. The SiO_2 on the front acts as a mask against plating as well as antireflection coating layer. Annealing was conducted at 400℃ for 30 min in forming gas (4% H_2 + 96% Ar). The performances of solar cells are confirmed independently by Fraunhofer Institute for Solar Energy Systems. EDS (Energy Dispersive Spectroscopy) was used to analyze Ni composition after annealing the Ni films on the silicon substrates.

2.1 Ni/Cu front contact formation

In order to study Ni/Cu contact system, 0.5 Ωcm FZ wafers were used since those wafers forms a rear ohmic contact with low contact resistance without additional boron diffusion under the rear metal contact (PERC Passivated Emitter and Rear Contact). The size of cell was 2 × 2 cm^2 on 4 inch diameter wafer. Ni contact was formed on the front grid pattern by electroless plating followed by annealing at 400℃ to allow formation of a nickel silicide in a tube furnace or a rapid thermal processing (RTP) chamber because the nickel is transformed to NiSi at 400℃(5). Cu was electroplated on the Ni layer using light induced plating method. Cu was electroplated on the Ni layer using light induced plating method. Cu electroplating solution was made up of commercially available acid sulfate bath and additives to reduce the stress of the copper. Cu electroplating solution was made up with commercially available acid sulfate bath and additives

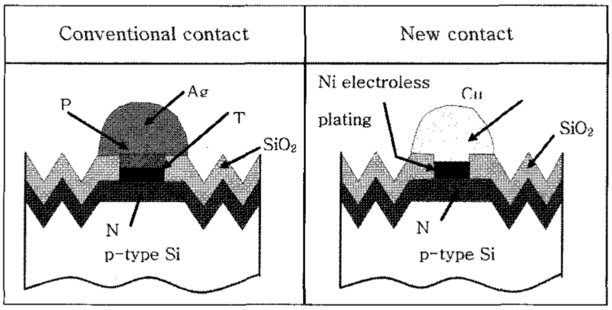


Fig. 1 Schematic diagrams of the conventional Ti/Pd/Ag contact system and new Ni/Cu contact system for high efficiency crystalline silicon solar cells.

to reduce the stress of the copper layer. Schematic diagrams of contact systems were shown in Fig. 1 Contact resistance of nickel silicide on an n$^+$ Si layer was measured using the transmission line model (TLM) method.

2.2 Fabrication of large area silicon solar cells

The solar cell size of 6.7 × 6.7 cm^2 was designed to study the effects of front contact system on the performance of large area solar cells since the current density through the front contact finger increases with the area of solar cells. FZ wafers with a resistivity of 2 cm were used since higher bulk resistivity produces higher current density due to longer diffusion length. Heavy boron diffusion through the contact hole was performed before metal contact formation on the rear side of the cell to reduce contact resistance and minority carrier recombination at metal and silicon interface. Two types of front contact were tried to reduce the series resistance. Shallow grooves were formed by the KOH etching in order to increase the aspect ratio of front contact before heavy phosphorous diffusion (Hybrid PERL/BCSC). Tapered contact structure was used to reduce power losses caused by increasing cell area and compared with the conventional PERL cell. It was found that series resistance due to the front grid finger was decreased without increasing shading losses. Solar cell structures used in this study are summarized in Fig. 2.

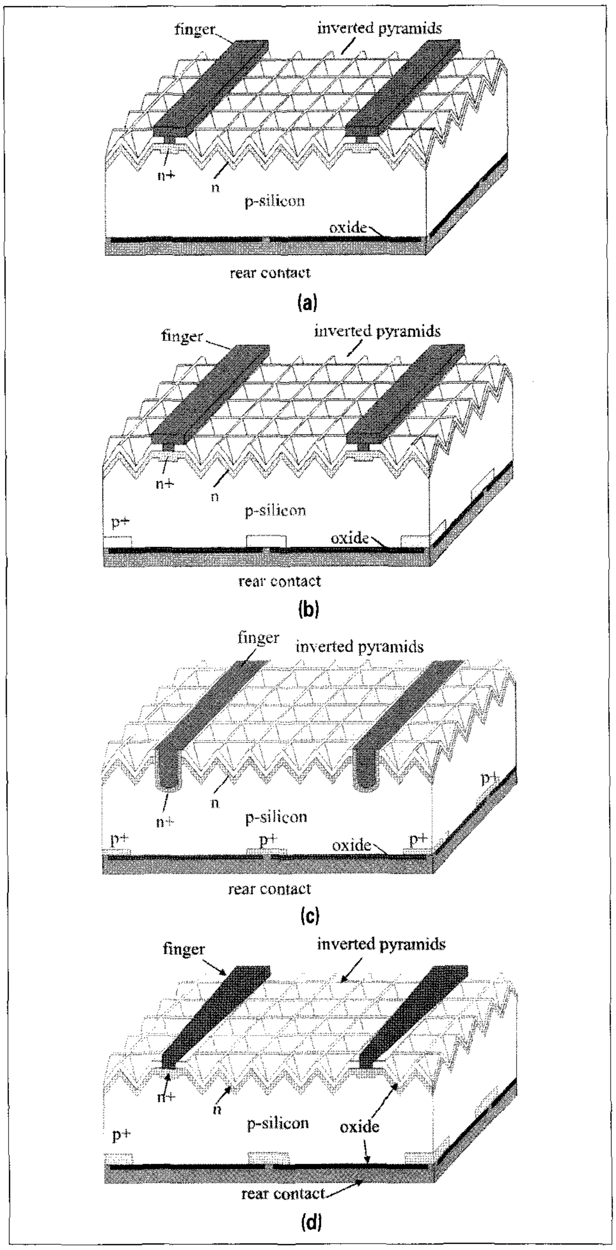


Fig. 2 Schematic diagrams of high efficient cells. (a) PERC, (b) PERL, (c) Hybrid PERL/BCSC and (d) PERL with tapered contact structure.

3. Performance of solar cells with plated Ni/Cu contact

The Ni plating solution is composed of a mixture of $NiCl_2$ as the main nickel source, NaH_2PO_2 as the reducing agent, and $(NH_4)_3C_6H_5O_7$ as a buffer and a mild complex agent for nickel. The nickel plating process is based on a catalytic oxidation-reduction reaction between nickel and hypophosphite ions. The chemical reaction can be viewed as the sum of two steps which occur simultaneously,

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{2-} + 2H^+ + H^-$$

$$2H^- + Ni^{2+} \rightarrow Ni + H_2$$

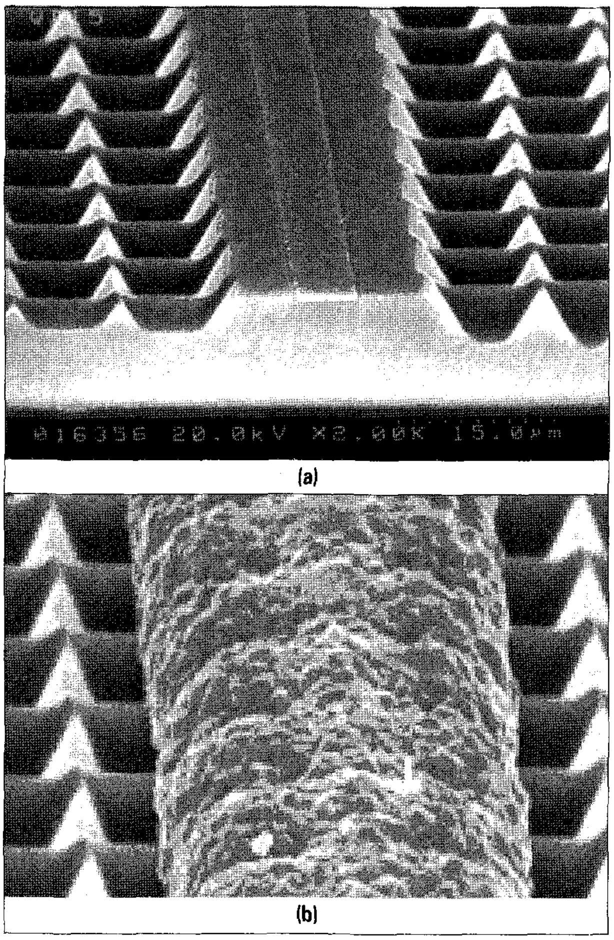
$$2H_2PO_2^- + 2H_2O + Ni^{2+} \rightarrow Ni + H_2 + 4H^+ + 2HPO_3^{2-}$$

Hydride ions (H^-) are produced at the catalytic surfaces via the dehydration of the hypophosphite (HPO_3^{2-}). These surface hydride ions react with the nickel ions (Ni^+) in solution reducing them to neutral nickel atoms bonded to the surface. Fig. 3 shows the Ni layer plated on the front grid pattern (a) and the electroplated Cu grid finger on the Ni layer (b). The plated Ni layer was annealed in nitrogen gas at 400℃ to form a NiSi.

The standard TLM is commonly used to model the planar metal-semiconductor contact, allowing important contact parameters such as contact resistance R_c (Ω), specific contact resistance Pc (Ωcm^2) and the semiconductor sheet resistance beneath the contact R_s ($\Omega/\square$). The transmission line consists of three sets of resistors representing the metal, semiconductor, and interfacial layers of a contact (6). The contact resistance between NiSi and n^+ Si can be extrapolated by the formula,

$$R_T = P_c d/Z + 2R_c$$

where R_T is the total resistance, and Rc is the contact resistance. The total resistance is measured for various contact spacings *d* and R_T is plotted as function of *d*. The intercept at $d = 0$ is $R_T = 2R_c$ giving the contact resistance. A test structure of the TLM method and a plot of R_T are shown in Fig. 4.



(a)

(b)

Fig. 3 SEM images of the Ni/Cu contact system for solar cell. (a) Electroless plated Ni layer and (b) electroplated Cu film on the Ni layer.

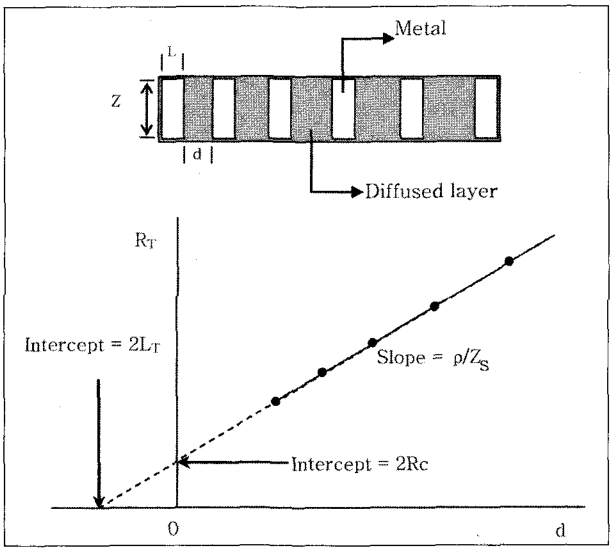


Fig. 4 A test structure of TLM method and a plot of total resistance as a function of contact spacing *d*.

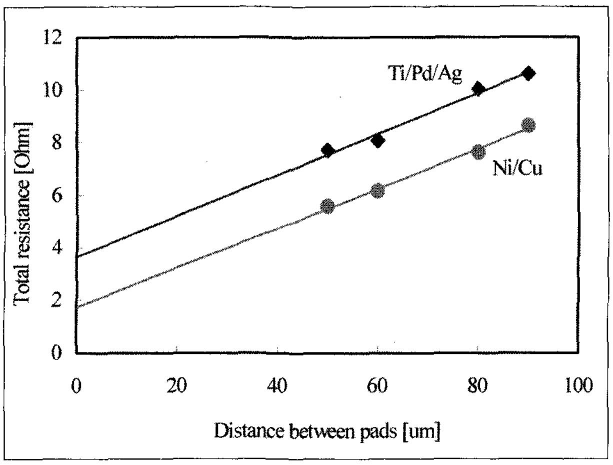
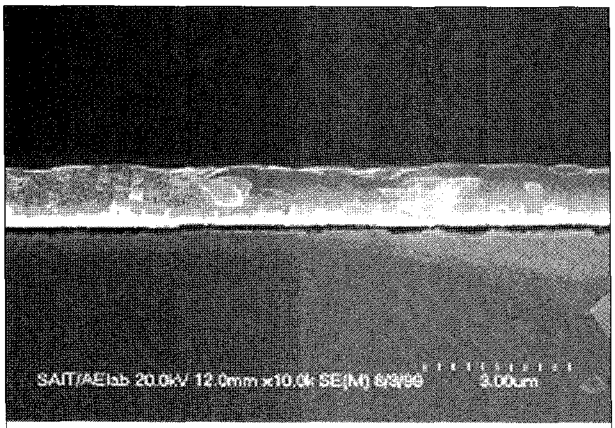
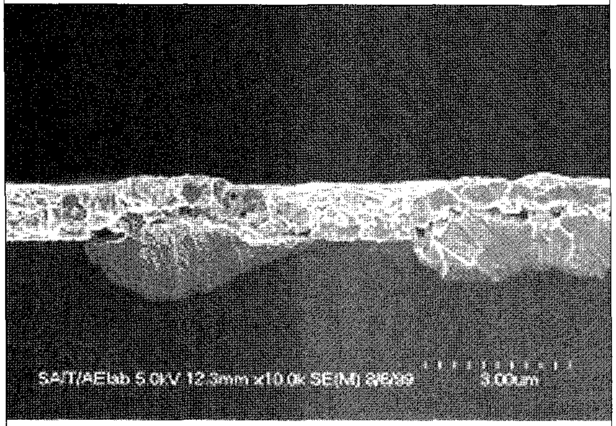


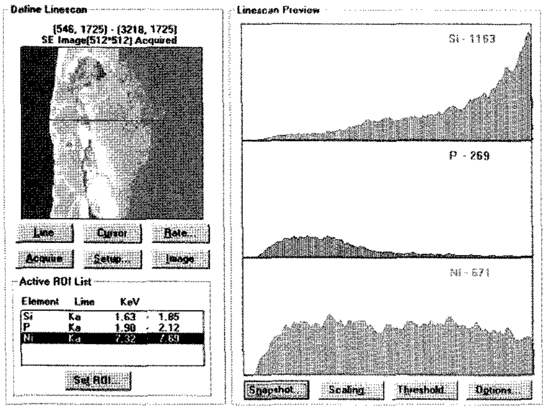
Fig. 5 Total resistance measurement of Cu/Ni/Si and Ag/Pd/Ti/Si contacts.



(a) As-deposited Ni on silicon substrate



(b) Ni was annealed at 600℃ for 30 sec.



Element	Line	KeV
Si	Ka	1.63 - 1.85
P	Ka	1.90 - 2.12
Ni	Ka	7.32 - 7.69

(c) EDS analysis of the plated Ni film (b)

Fig. 6 SEM images of plated Ni films before (a) and after (b) annealing at 600℃ for 30 sec. (c) shows the composition profiles along the straight line in the SEM image.

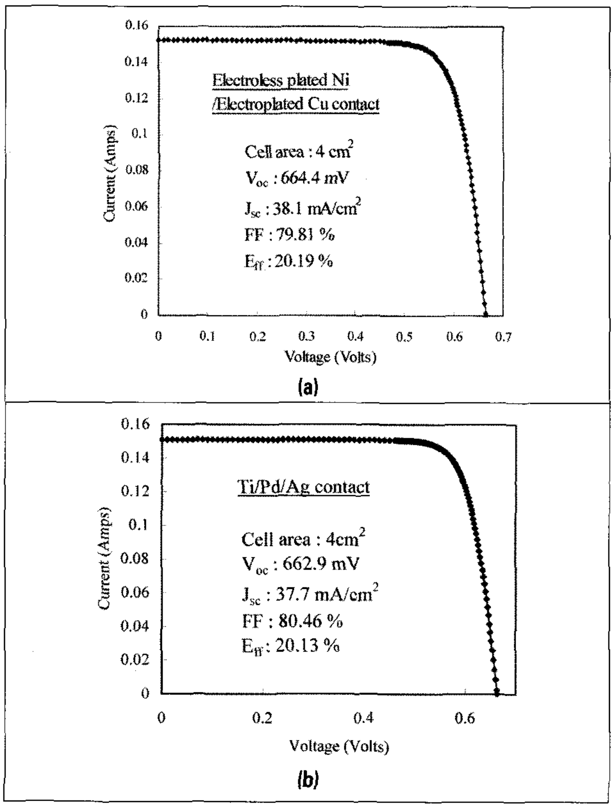
The intercept at $d = 0$ is $R_T = 2R_c$ giving the contact resistance. Contact resistance of Cu/Ni/Si and Ag/Pd/Ti/Si were measured by the TLM method as shown in Fig. 5. Contact resistivity of Cu/Ni/Si system was characterized to be 3.5×10^{-5} Ωcm^2 which is even lower than that of Ag/Pd/Ti/Si system (7.3×10^{-5} Ωcm^2). A contact resistivity less than 1×10^{-3} Ωcm^2 was found to give sufficiently low power loss for one sun applications. It was therefore found that NiSi was suitable for high efficiency solar cell application.

Fig. 6 shows that nickel silicide forms non-uniformly if the annealing temperature is too high. The thickness of the silicide was measured to be about 3 ㎛ which is thick enough to penetrate the emitter and make shunting path. The phosphorous was introduced in the Ni film during the plating because the plating solution contains NaH_2PO_2 as a reducing agent.

Fig. 7 compares the performance of solar cell with Ni/Cu contact system with that with Ti/Pd/Ag contact system. The structure of solar cell was PERC type in which the aluminum sintered layer was replaced by a passivating silicon dioxide layer to reduce surface recombination velocity at rear surface. Cell parameters of the PERC cell with Ni/Cu contact system are V_{oc} = 664.4 mV, J_{sc} = 38.1 mA/cm^2, fill factor (FF) = 79.8%, and efficiency (E_{ff}) = 20.19%. The series resistance (R_s) of the cell with Ni/Cu contact system is 0.16Ω and the cell with Ti/Pd/Ag is 0.15Ω. It is interesting to note that the simple and low cost Ni/Cu contact system showed performance equivalent to the expensive Ti/Pd/Ag contact system.

4. Improvement of front contact structures for large area solar cells

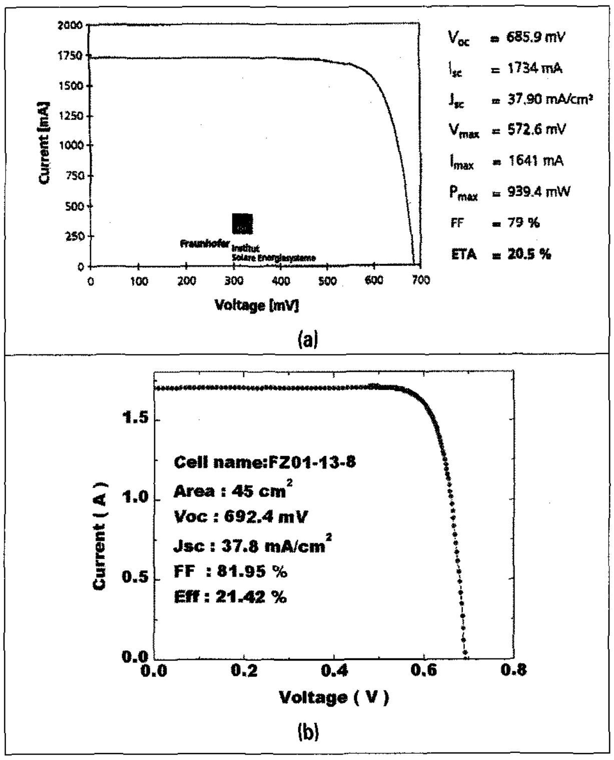
The resistivity of plated metal contact system is generally much lower than that of screen printed metal contact because pure metal is deposited during the plating. And the plated metal contact has low contact resistance because it is formed on the surface of the diffused emitter whereas the screen printed contact is formed by etching the surface of emitter. As a result of low contact resistance and resistivity of fingers, the plated metal contact gives high fill factor. Fig. 8 shows



(a)

(b)

Fig.7 Light I-V curves of a solar cell with (a) electroless plated Ni/electroplated Cu contact system and with (b) evaporated Ti/Pd/Ag contact system.



(a)

(b)

Fig. 8 Current-Voltage characteristics of SiO_2 coated PERL cells. The efficiency of cell (a) was measured at Fraunhofer Institute of Solar Energy Systems (AM1.5 spectrum, 100 mW/cm², 25℃, 45.75 cm² cell area). Solar cell (b) with a tapered contact structure was measured using I-V tester calibrated with solar cell (a).

the performances of large area PERL cells. Boron was heavily doped under the rear metal contact. The sheet resistance of layer diffused with boron ranged from 10 to 20 Ω/□. Heavy doping under the rear metal reduces recombination velocity by blocking minority carrier diffusion and contact resistance, which enhances open circuit voltage. With 110 nm thick SiO_2 as an antireflection coating layer, the efficiency of 20.5% has been demonstrated at Fraunhofer Institute for Solar Energy Systems for a cell with an area of 45 cm² as shown in Fig. 8(a). The fill factor was reduced to 79% due to high series resistance as the cell size was increased from 4 cm² to 45 cm². The R_{series} of a solar cell usually degrades the output power by decreasing fill factor and short circuit current. R_{series} is the sum of several components, such as rear metal contact resistance, emitter sheet resistance, substrate resistance, upper contact resistance, and grid resistance. New contact design, tapered contact structure, was introduced to increase the fill factor of the large area solar cell without hurting the short circuit current density as shown in Fig. 8(b). It is interesting that the fill factor of the solar cell with tapered contact increased to 81.95% with almost same short circuit current density producing a conversion efficiency of 21.42% on 45 cm² cell. There are several ways to form tapered contact structure during the plating process. The optimization of contact geometry was fulfilled by using the Cuevas's iteration method (7). With an antireflection coating of ZnS/MgF_2, the efficiency of over 22% becomes feasible since 3% increase of short circuit current can be expected.

5. CONCLUSION

Expensive Ti/Pd/Ag contact was replaced by low cost Ni/Cu contact without sacrificing cell performance. Nickel silicide formation at the interface enhanced stability and reduced the contact resistance resulting in a conversion efficiency of 20.2% on 0.5 Ωcm FZ wafer. Formation of Ni/Cu contact by plating is expected to provide cost effective metallization of high-efficiency solar cells suitable for mass production without efficiency loss. Tapered contact structure has also been applied to large area solar cells with $6.7 \times 6.7\text{cm}^2$ in order to reduce power losses by the front grid. High-efficiency solar cell with an efficiency of 21.4% on 45cm^2 area was obtained by optimizing the front contact design and processing. The contact structure is expected to be applied to low cost commercial solar cells if the photolithography process for opening silicon dioxide under the front metal is replaced by other inexpensive process.

REFERENCES

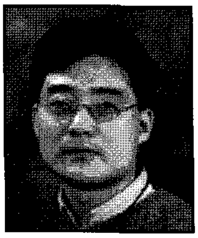
1. J. Zhao, A. Wang, M. Green and F. Ferrazza, Appl. Phys. Lett., vol.73, 1998, p.1991.
2. Paul D. Maycock, "Photovoltaic Technology, Performance, and Cost 1995-2010", January 2000.
3. S. P. Murarka, in "Silicides for VLSI applications" (Academic press, 1983), p.78.
4. Yaozhi Hu and Sing Pin Tay, *J. Vac.Sci.Technol.* **A16**(3), 1998, p.1820.
5. S. R.Das, in Proceedings of Materials Research Society Symposium, April 1996, edited by K. N. Tu. **427**p. 541.
6. Dieter K. Schroder and Daniel L. Meier, *Solar cell contact resistance-A review*, IEEE Transactions on electron devices, **ED31:5**, 1984, p. 637.
7. A. Cuevas and D. A. Russel, "Co-optimization of the emitter region and metal grid of silicon solar cells", Prog. Photovolt. : Res. Appl., vol.8, 2000, pp.603-616.

김 동 섭

1988-1990 : KAIST 재료공학과 석사
1990-1994 : KAIST 재료공학과 박사
1994-1998 : 삼성종합기술원 선임연구원
1998-1999 : University of Illinois at UC Post Doc
2001-2003 : Georgia Institute of Technology 선임연구원

2003-현재 : 세종대학교 전자공학과 교수
(E-mail : dskim@sejong.ac.kr)

김 정



1998. 8 : 서울대학교 대학원 졸업(이학박사학위 취득)
1995. 8 ~ 1996. 8 : 서울대학교 기초과학연구원 조교
1998. 9 ~ 2000. 8 : 삼성종합기술원 반도체소자랩 연구원
2000. 9 ~ 2004. 2 : 삼성SDI 중앙연구소 책임연구원

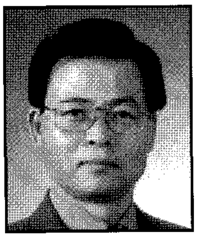
2004. 3 ~ 현재 : 세종대학교 전자공학과 조교수
(E-mail : kimjeong@sejong.ac.kr)

이 은 주

1995 ~ 1999 : 서울시립대학교 재료공학 석사
1999 ~ 2004 : 삼성SDI 중앙연구소 전임연구원

2004 ~ 현재 : 세종대학교 박사과정
(E-mail : eunjoo@sju.ac.kr)

이 수 홍



1991 : 호주 UNSW 전자공학과 박사
1992.8 ~ 1993.12 : 독일 막스플랑크 고체연구소 객원과학자
1994.1 ~ 2002.2 : 삼성종합기술원, 삼성SDI 태양전지 팀장

2002.3 ~ 현재 : 세종대학교 전자공학과 교수,
전략에너지연구소 소장
(E-mail : shl@sejong.ac.kr)