Int. J. Electrochem. Sci., 7 **(2012)** 10711 - 10721

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

An Investigation of the Mechanisms of Light-Induced Nickel Plating on P-type Silicon Substrates

Yu-Han Su[1], *Wei-Yang Ma*[1,*], *Tsun-Neng Yang*[1], *Shan-Ming Lan*[2]

[1] Institute of Nuclear Energy Research, Atomic Energy Council, Executive Yuan, Taiwan
[2] Department of Electronic Engeering, Faculty of Engineering, Chung Yuan Christian University, Taiwan
*E-mail: pony@iner.gov.tw

Received: 26 September 2012 / *Accepted:* 18 October 2012 / *Published:* 1 November 2012

In the process of silicon solar cell production, the fabrication of plated Ni/Cu contacts is regarded as the next generation of metallization processes and has the potential to replace the screen-printing technology. In this paper, we discuss the mechanisms of Light-Induced Nickel Plating (LINP) on semiconductors, which can be applied for Ni/Cu metallization. Our experiments show that when a p-type silicon with or without n/p structure, which has been previously subjected to aluminum metallization on the back, is immersed in a plating bath, metal ions are reduced on the front surface of the semiconductor as soon as illumination starts. The results demonstrate that the mechanisms of light-induced nickel plating are not entirely due to the potential difference induced inside the n/p junction of the semiconductors, as stated by other authors. The main deposition principle may be related to the potential differences separately induced on the metal/solution interface, as well as on the semiconductor/solution interface under thermal equilibrium. To the best of our knowledge this has not yet been mentioned in the literature related to plating. This study discusses the techniques and methods developed to overcome the current shortcomings with electroless plating and electroplating in the solar cell process. Furthermore, the nickel films formed by LINP in a fast and simple process, were analyzed using SEM as well as XPS and shown to display uniform metal surfaces and high intrinsic quality.

Keywords: Light-Induced Plating; Light-Induced Nickel Plating; Ni/Cu; LIP; plating; metallization

1. INTRODUCTION

Metallization is one of the key steps in solar cell fabrication. This process is developed to lower production cost and increase efficiency. Currently, in the silicon solar cell industry, screen-printing is the main contact process, because it is easy, fast producing, and its performance close to the Ti/Pd/Ag metal evaporation technique. However, the metallization produced by screen-printing has a low aspect ratio and high specific contact resistance that restricts solar cell efficiency.

High efficiency, low cost and wafer thinning are future trends in the solar cell industry. However, the low aspect ratio, high specific contact resistance, and the “pressing” process of screen-printing contact technology hinder the development of high efficiency silicon wafers. Therefore, the fabrication of Ni/Cu metal contacts has been assessed as the next generation of contact technology for solar cells and is a good solution to further enhance the efficiency with low specific contact resistance. It also has the advantages of low material cost, “non-press” process and is suitable for mass production. The general standard process of Ni/Cu contact fabrication is that a nickel metal film is first plated onto the front of the solar cell, then through the silicidation process, the residual nickel is removed, and finally a copper and a tin metal film, which serve as the conduction layer and act to prevent oxide formation respectively, are sequentially plated [1-9].

The two most common types of chemical plating processes are electroplating and electroless plating. Electroplating is a well-developed technology but can only work on conducting materials rather than semiconductors. Therefore, the electroless plating technique is extensively utilized in the Ni/Cu plating process of silicon solar cells [10-14]. Electroless plating is an auto-catalytic chemical process used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid workpiece, such as metal or plastic with a proper pre-plating catalyst. This technique makes it possible to plate metal on a non-conductive workpiece. The process relies on the presence of a reducing agent which reacts with the metal ions to form metal films and the pre-treatment procedure of the surface catalyst. However, knowledge of the process of surface catalysis is known by each Ni/Cu development team, and the complexity of the process also increases the cost.

Light-Induced Plating (LIP), a novel plating technique, has been widely developed by Fraunhofer ISE since 2006. A wafer with an n/p junction and Al rear contact that is fabricated by screen-printing is immersed in a plating bath. At the same time, a protective potential is imposed between the Al rear contact and an auxiliary anode in order to prevent the aluminum from being eroded chemically. The deposition mechanism of LIP is attributed to the built-in potential on the n/p junction. In this way, the protective potential also promotes the deposition process. This is a promising technique due to its high plating rate and there being no need for a surface catalyst as in traditional electroless plating. Further details have been published in many studies [15-21]. Aside from Fraunhofer LIP, there is another technique, electroless nickel plating, carried out through illumination that is referred to as Light-Induced Electroless Plating (LIEP) [22]. Although this improves the quality of metal films, it still involves the complex process of electroless plating.

In this study, a progressive technique called Light-Induced Nickel Plating (LINP) is presented, and is shown to be a more appropriate method for nickel plating on semiconductor substrates. In our study, a simple and fast nickel deposition process was utilized to successfully form contacts on the surface of silicon substrates which were subjected to an aluminum rear contact within the nickel plating solution under illumination. When the prepared substrate is immersed in the plating solution, the nickel film begins to form as soon as illumination starts. It is worth mentioning that the process works not only for the p-type silicon substrate with n/p structure but also for the p-type silicon substrate itself. This experimental results show that the plating is not reliant only on the built-in potential of n/p junction. We consider the main mechanism of the LINP plating process to occur is due to the interfacial potential induced at the interface between the aluminum electrode and plating solution. Since the potential is induced by interfacial electrochemistry, LINP can be applied on a p-type silicon substrate directly without the requirement of an n/p junction, reducing agent in the bath, additional applied voltage, surface pre-treatment, etc. Generally speaking, this technique has the advantages of being a simple process, fast plating and low cost potential.

2. EXPERIMENTAL PROCEDURE

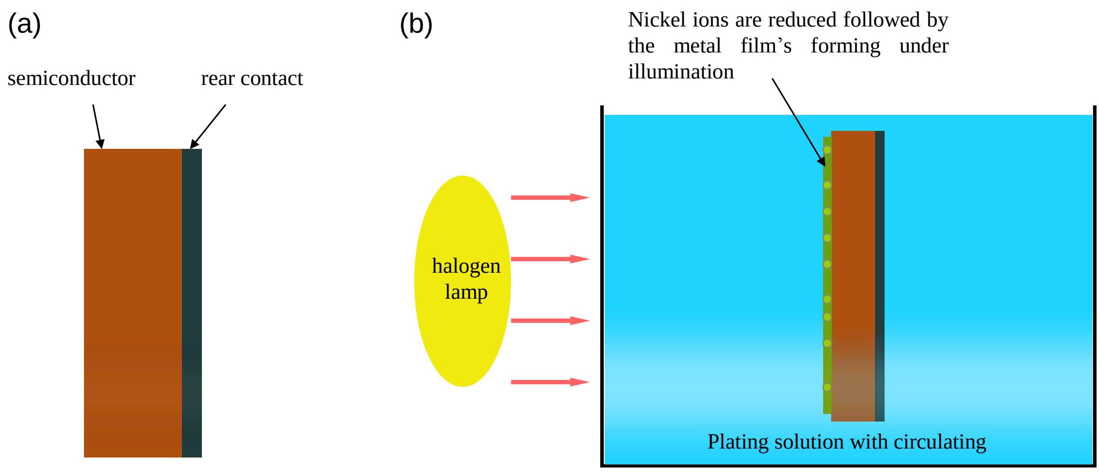


Figure 1. Experimental preparation for the LINP process. (a) schematic representation of the prepared specimen which contains the semiconductor substrate and the aluminum contact formed by the e-gun or screen-printing process. (b) The experimental setup for the plating process. The prepared specimen is immersed in a circulating plating bath. Nickel ions will be reduced and followed by the formation of a metal film on the front surface under illumination.

A p-type silicon substrate with and without n/p structure were used in this experiment. After a pretreatment for cleaning and chemical etching, the substrates were subjected to contact formation through Al e-gun evaporation or Al screen-printing under the respective firing conditions. In our case, the aluminum paste in screen-printing process was purchased from the AgPRO Company in Taiwan. The above processed substrates serve as specimens for the LINP process, as shown in Fig. 1(a). After this, a circulating plating bath containing nickel chloride and a boric acid aqueous solution was prepared. A halogen lamp was also selected for use in this experiment. The whole experimental setup is illustrated in Fig. 1(b). Before the start of the plating process, the prepared specimen was immersed in the circulating plating bath, after which the halogen lamp was turned on to illuminate the plated surface directly. Then nickel deposition started immediately. The deposition period in our experiment was about 1-2 minutes. Finally, we removed the specimen, rinsed it in DI water and dried it. This was the whole LINP plating process.

After nickel plating the finished sample was processed by a heat treatment of 400℃ for 30 seconds in an RTA furnace, during which nickel silicide formed between the silicon and the metal. Finally, residual nickel that did not react to silicon was removed chemically by a solution of sulfuric acid and hydrogen peroxide. The films were analyzed using SEM and XPS measurements.

In order to prove that a potential drop is generated across the rear contact and the plating solution, a simple experiment is designed, as shown in Fig. 2.

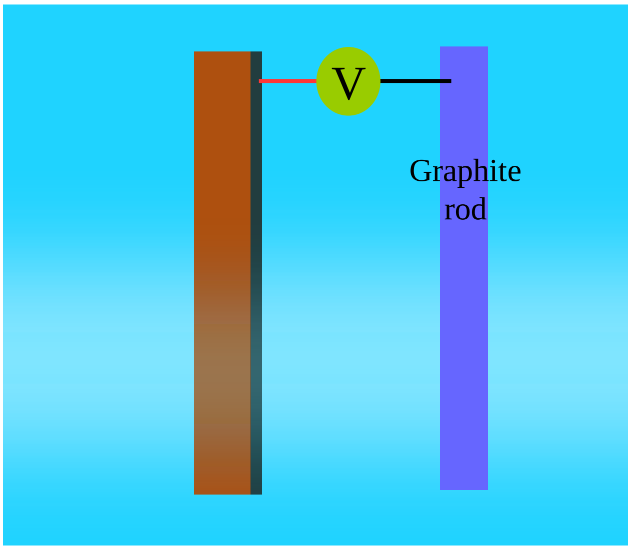


Figure 2. Experimental setup for measuring the voltage between the rear contact and the graphite rod. Three contacts formed by screen-printed aluminum, e-gun evaporation aluminum, and e-gun evaporation of Ti-Pd-Ag are measured.

A voltmeter was connected between the rear metal contact and the applied graphite rod which were both immersed in the solution. In this experiment, three types of rear metal contacts, including e-gun evaporation Al, screen-printed Al and e-gun evaporation Ti/Pd/Ag were used for the comparison. The measured voltage values mainly included the interfacial potential for the metal/solution and graphite/solution.

3. RESULTS

The LINP process was successfully used to plate nickel onto the substrates of p-type silicon and with n/p structure which were previously subjected to rear contact formation by e-gun evaporation of Al or screen-printing of Al. During the plating process, however, chemical erosion occurred on the Al electrode when using the e-gun evaporation. In contrast, there were only partial specimens that had the chemical erosion on the screen-printed Al electrode. The surface morphology and cross-sectional SEM images of the nickel films on p-type silicon substrate with screen-printed Al are shown in Fig. 3(a)-(c). The same results are also shown for the p-type silicon substrate with e-gun Al evaporation, and for n/p structure substrate with e-gun or screen-printed Al contacts. The XPS measurements, as shown in Fig. 4, show the film’s composition. The deposition period is only 1-2 minutes, which is a fast plating rate compared to electroless plating.

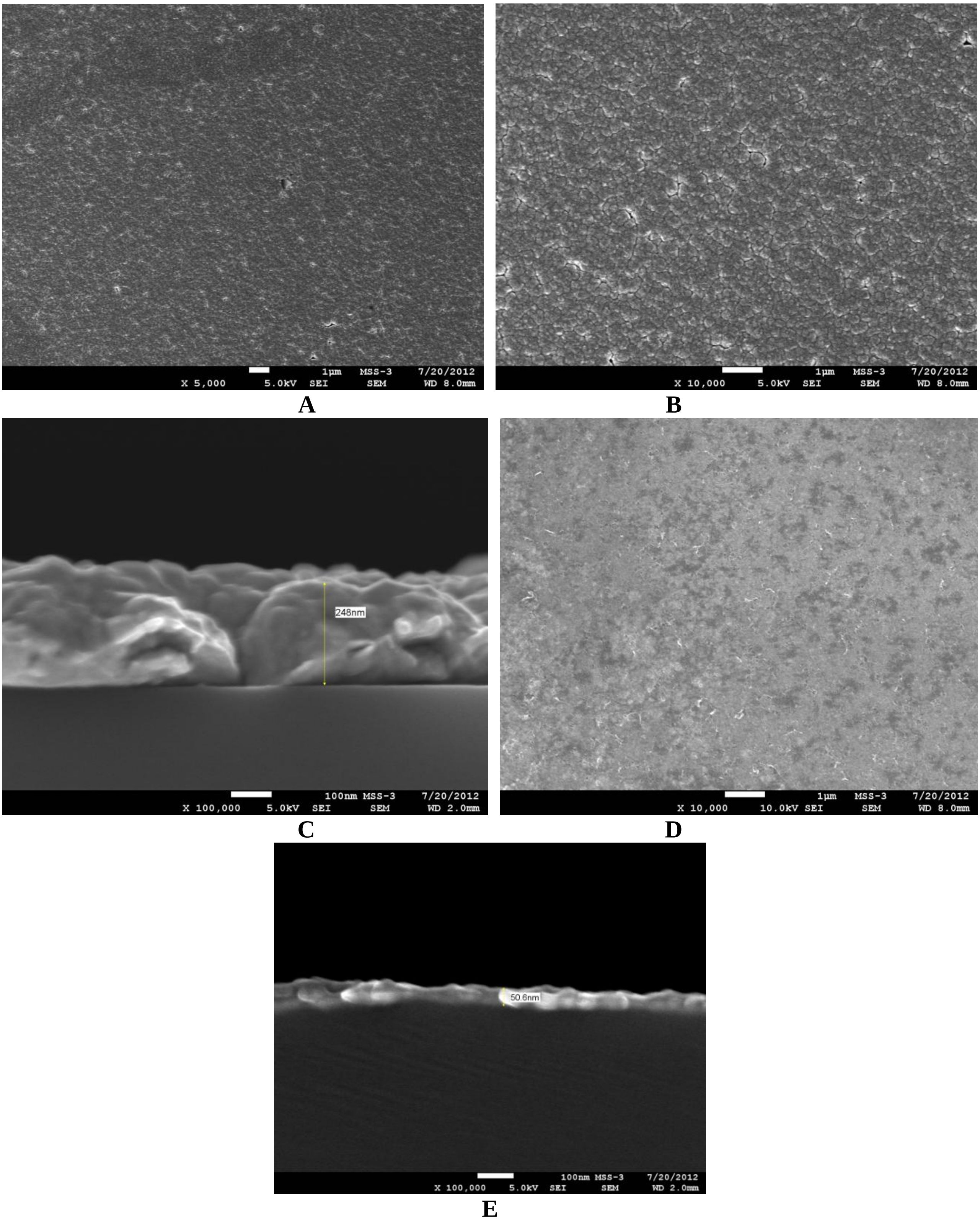


Figure 3. SEM images of nickel films formed by LINP process using a substrate of p-Si wafer with screen-printed Al contact. (a) A surface topography of the nickel films at 5,000x. (b) surface topography of the nickel films at 10,000x. (c) cross-sectional image of the nickel films at 100,000x. (d) top view of nickel silicide at 10,000x. (e) cross-sectional image of nickel silicide at 100,000x.

After thermal processing, a nickel silicide layer is formed, and its morphology as well as cross-sectional SEM images are shown in Fig. 4(d)-(e). The measured voltage differences between the rear metal contacts and graphite rods are listed in Table 1.

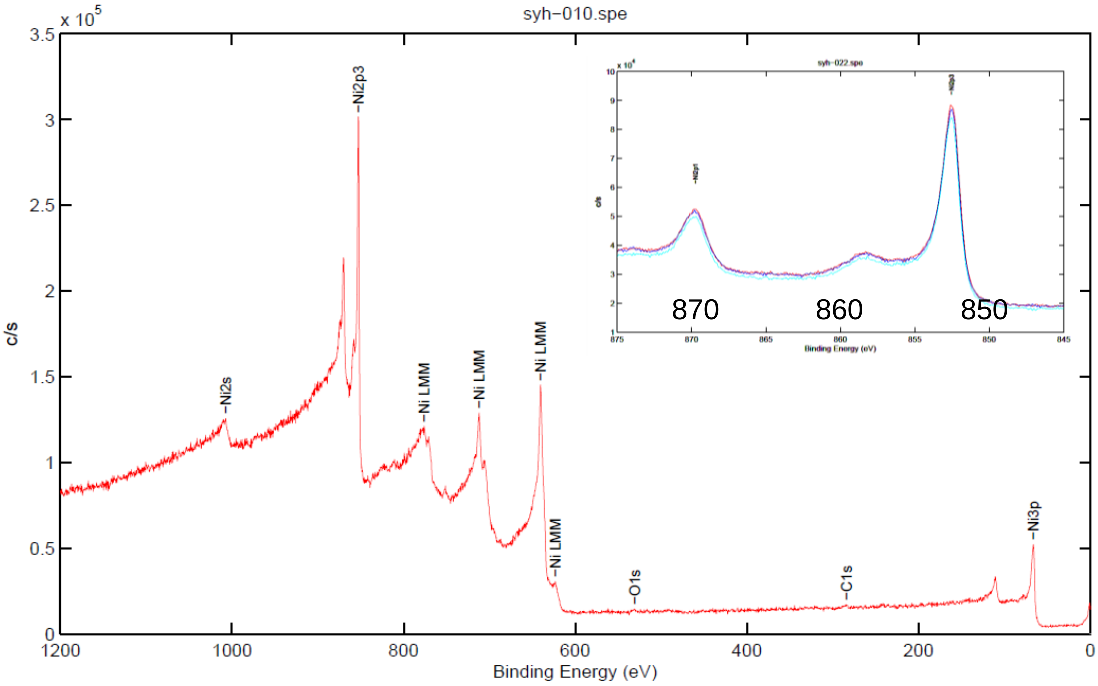


Figure 4. XPS measurements of the whole and its part (binding energy ranges from 845 to 875 eV) of the nickel films using the LINP process.

Table 1. Experimental results showing the measured voltage differences between the three different types of rear metal contact and the graphite rod.

Rear metal type	Measured voltage difference (V)
e-gun Al	-1.2
screen-printed Al	-0.8
Ti/Pd/Ag	-0.32

4. DISCUSSION

The mechanism of the light-induced nickel plating process carried out on the p-type silicon substrates, with or without n/p structure, is discussed as follows. We consider that there is a voltage drop at the interface between the metal and the plating solution that is induced due to the difference in the Fermi level on either sides. Theoretically, the equilibrium condition for the redox reaction between the metal and solution is: E_F (metal) = E_F (solution) [23, 24]. This condition will cause bending of the energy levels and a potential difference across the interface. Fig. 5 shows a schematic representation of the interface with the electric field between the metal surface and the solution.

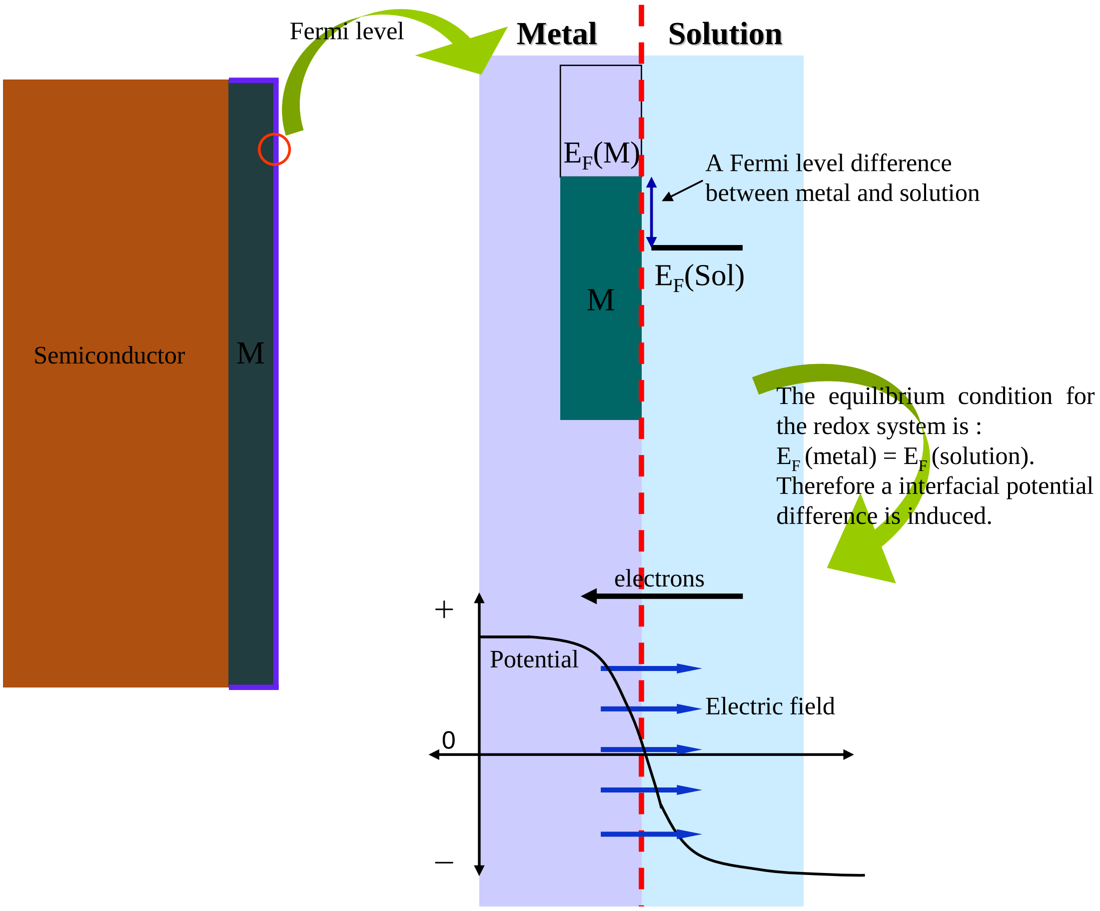


Figure 5. Schematic representation showing the interfacial potential difference that is induced due to the Fermi level difference between the metal and the solution. The potential difference at the metal/solution interface is induced by the equilibrium condition of E_F (metal) = E_F (redox).

The electric field is considered to play a critical role in the LINP process, which supplies a voltage source in the system. Fig. 6 shows more details of the metal/solution interface by using electrochemistry theory [23]. It illustrates the charge and potential distribution when the system is under equilibrium. When the metal surface carries excess positive charges, there attracts solution anions in contact with the metal, which is referred to as “specifically adsorbed”, also called the inner Helmholtz plane (IHP). In addition, solvated anions also will approach the IHP and form the layer, called outer Helmholtz plane (OHP). Therefore, there exists a potential across the metal/solution interface which includes the IHP and OHP, which can only be evaluated indirectly through an additional probe, as shown in the experimental setting in Fig. 2. In fact, the measured voltage should include the total potential mainly on the interfaces of the metal/solution and graphite/solution. And the total potential can determine whether the nickel plating process will happen or not. As Table 1 shown, the difference in the experimental potential between the e-gun Al and Ti/Pd/Ag is 0.88 V (i.e. 1.2(V) - 0.32(V)). Based on the results, we deduce that the voltage drop between the e-gun Al contact and solution interface is greater than 0.88V and it is very possible to reduce the nickel ions.

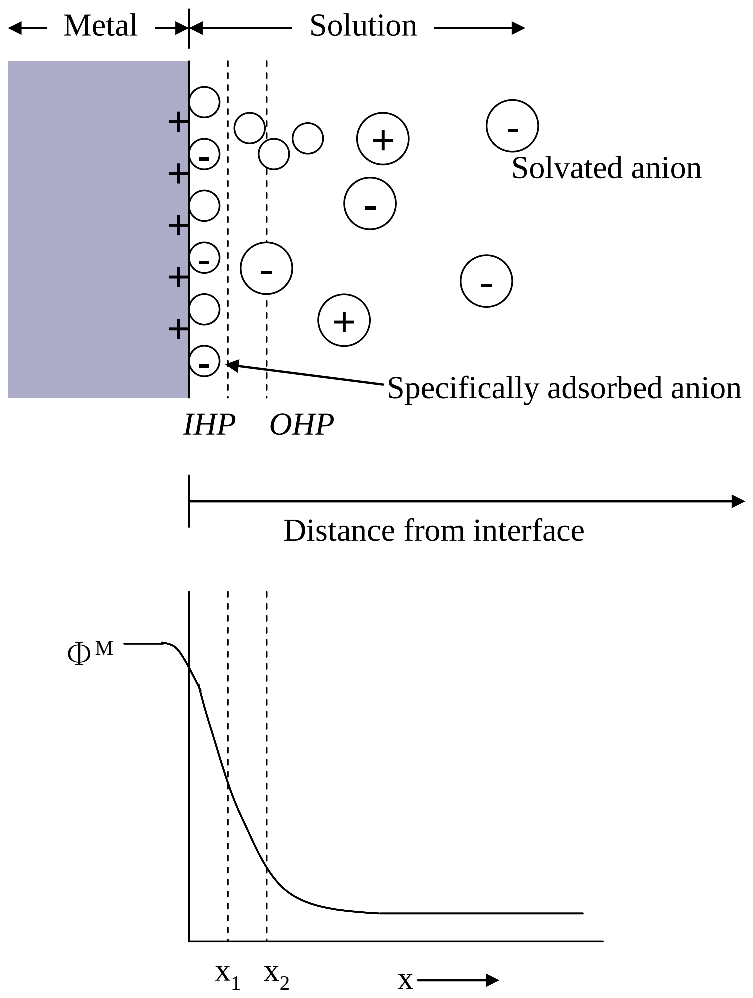
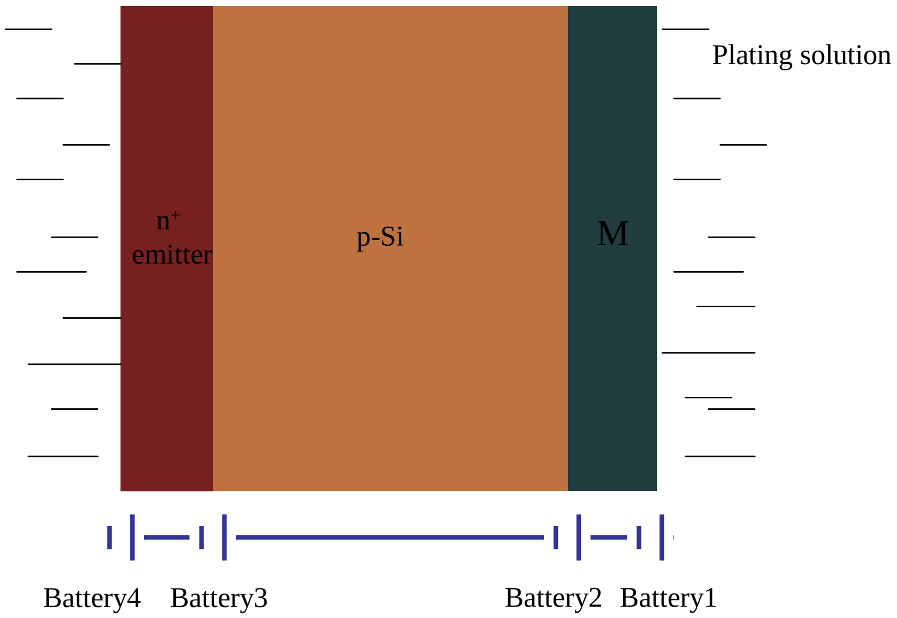


Figure 6. Model of the charge and potential distribution at the metal/solution interface [23].

Regarding the theoretical calculation, the potential difference is relative to both sides of the Fermi level of the metal and the solution [25]. However, it is not easy to obtain the Fermi level of the plating solution because it is necessary to consider the complexities of the chemical system [26]. Therefore, this is not evaluated in this study. Nevertheless, it is very crucial to the LINP process to make the plating technique optimize. For the same reason, there also exists a voltage drop at the interface between the semiconductor/solution on the front side of the semiconductor. Furthermore, a BSF layer across the aluminum and silicon wafer is believed to play a partial role in the LINP deposition process. This means that the nickel deposition process may be mainly attributed to the total summation of the interfacial potential of the metal/solution, semiconductor/solution, BSF, and n/p junction in an n/p structure substrates. As shown in Fig. 7, the interfacial potential can be regarded as batteries that are series connected in the plating solution. When illumination is applied, the semiconductor becomes conductive and the current begins to flow. The nickel ions are reduced on the cathode’s semiconductor surface.



Battery1: metal/solution interfacial potential
Battery2: BSF with Al contact
Battery3: n/p junction within n/p solar cell
Battery4: semiconductor/solution interfacial potential

Figure 7. Schematic representation of the full electrochemical system by a series of interfacial potentials in a plating solution.

Different metal contact materials have different characteristics based on their intrinsic properties, the lattice structure, and the crystal face of surface. Therefore, there will be different potential drops between the metal/solution due to the different Fermi level of the metals. As shown in Table 1, the experimental voltage between the e-gun Al and the graphite rod is -1.2V, and it is -0.8V between screen-printed Al and the graphite. There is a difference of 0.4V between screen-printed Al and the e-gun evaporation Al. The results show that there are different voltage drops on the surfaces of the two different types of Al rear metal contacts. This should affect the plating conditions in the LINP process. Fortunately, the LINP has been successfully used to plate nickel films on semiconductor substrates with rear e-gun Al and screen-printed Al contacts. On the other hand, in the experiments there was always erosion phenomenon taking place on the e-gun Al metals during the plating process, however, the phenomenon was not obvious on the screen-printed Al metals, and some screen-printed Al metals even remain intact. We think that the erosion effect is dependent on the properties of the metal. The screen-printed Al is more unstable in chemical reactions. Although the screen-printing contacts appear unstable, it is more exciting that there must exist a chemical equilibrium for the formation of metal films without rear contact erosion because it has been successfully produced in our processing. In our opinion, this technique can be optimized by adjusting all conditions of the electrochemical system and the Fermi levels, including the metal, the semiconductor, and the solution. It is also supposed that the erosion phenomenon of aluminum can be improved by utilizing the best electrochemical conditions.

In our experimental process, the system was initially at room temperature but was gradually heated due to the light irradiation. This did not influence the film quality in the first round of plating because the plating period was only about 1-2 minutes. The temperature variation was not enough to influence the quality of the metal film. Aside from this, the deposition behavior was very sensitive to the circulation condition of the solution, which is reasonable because deposition mainly occurs in a chemical system. This technique has so far been used for the deposition of a whole area of nickel film. Future work will be carried out to pattern the front side of the solar cell with buses and grids, for which a laser process is considered [27]. Furthermore, the cost of this process can be further reduced by using sunlight rather than halogen lamps.

Consequently, the LINP may be a promising technique for Ni/Cu plating due to its simple process, fast plating rate and low cost potential.

5. CONCLUSION

We reveal a progressive process for nickel plating by using the LINP technique and also outline the mechanism for LINP deposition. Nickel films have been plated using a fast and simple process without the need for a reducing agent, surface pre-treatment, additional voltage or special heating requirements. We propose that the interfacial potential which is induced between the aluminum metal and the plating solution leads to the nickel deposition. The plated nickel films are shown to display uniform surfaces. Furthermore, nickel silicide can be formed by annealing and further thickened by copper electroplating. This LINP technique could be further improved by optimizing the conditions of the plating bath and aluminum paste to achieve the best result in the electrochemical system.

ACKNOWLEDGEMENT
The authors thank the colleagues of the epitaxial group all members for all technical assistance concerned with this work. We also thank Chin-Chang Shen for the XPS measurement.

References

1. D. S. Kim, E. J. Lee, J. Kim, and S. H. Lee, *J. Korean Phys. Soc.* 45 (2005) 1208.
2. Holger Knauss, Barbara Terheiden, Peter Fath, *Sol. Energy Mater. Sol. Cells* 90 (2006) 3232.
3. Vikrant A. Chaudhari, Chetan S. Solanki, *Sol. Energy Mater. Sol. Cells* 94 (2010) 2094.
4. B. S. Richards, *Prog. Photovolt. Res. Appl*. 12 (2004) 253.
5. H. H. Kuehnlein, N. Koesterke, G. Cimiotti, E. Hartmannsgruber, N. Buerger, H. Nussbaumer, D. Luetke-Notarp, M. Becker, 24th European Photovoltaic Solar Energy Conference (2009) 282.
6. S Bandopadhyay, U Gangopadhyay, K Mukhopadhyay, H Saha, A P Chatterjee, *Bull. Mater. Sci*. 15 (1992) 473.
7. S. H. Lee, Solar Energy 83 (2009) 1285.
8. E. J. Lee, D. S. Kim, S. H. Lee, *Sol. Energy Mater. Sol. Cells* 74 (2002) 65.
9. S. H. Lee, *J. Korean Phys. Soc*. 39 (2001) 369.
10. Miles V. Sullivan, John H. Eigler, *J. Electrochem. Soc*. 104 (1957) 226.
11. Hitoo Iwasa, Masami Yokozawa, Iwao Teramoto, *J. Electrochem. Soc*. 115 (1968) 485.

12. C. Boulord, A. Kaminski, Y. Veschette, M. Lemiti, *Mater. Science Eng*. B 165 (2009) 53.
13. A. E. B. Marques, S. G. Santos Filho, S. Martini, *Phys. Stat. Sol*. 4 (2007) 256.
14. C. Boulord, A. Kaminski, B. Canut, S. Cardinal, M. Lemiti, *J. Electrochem. Soc*. 157 (2010) H742.
15. Alison Lennon, Yu Yao, Stuart Wenham, *Prog. Photovolt.: Res. Appl*. (2012)
16. N. Bay, V. Radtke, M. Aleman, J. Bartsch, S. W. Glunz, 24th European PV Solar Energy Conference and Exhibition (2009) 1434.
17. A. Mette, C. Schetter, D. Wissen, S. Lust, S. W. Glunz, G. Willeke, IEEE 4th World Conference on Photovoltaic Energy Conversion 1 (2006) 1056.
18. J. Bartsch, V. Radtke, C. Schetter, S. W. Glunz, *J. Appl. Electrochem*. 40 (2010) 757.
19. M. Horteis, S. W. Glunz, *Prog. Photovolt.: Res. Appl*. 16 (2008) 555.
20. M. Aleman, N. Bay, D. Barucha, S. W. Glunz, R. Preu, *Galvanotechnik* 100 (2009) 412.
21. M. Horteis, J. Bartsch, S. Binder, A. Filipovic, J. Merkel, V. Radtke, S. W. Glunz, *Prog. Photovolt.: Res. .Appl*. 18 (2010) 240.
22. David Minsek, US Patent No. 427581, USA, 2011.
23. Rüdiger Memming, Semiconductor Electrochemistry, Weinheim, Germany, 2002, Chapter 4, 5.
24. Wolfgang Schmickler, Elizabeth Santos, Interfacial Electrochemistry, second ed., London, New York, 2010, Chapter 1,3,4,5.
25. Wolfgang Schmickler, Elizabeth Santos, Interfacial Electrochemistry, second ed., London, New York, 2010, p. 35.
26. Rüdiger Memming, Semiconductor Electrochemistry, Weinheim, Germany, 2002, Chapter 3.
27. P. Engelhart, *Proc. of SPIE*, 7202 (2009) 72020S-1.