[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 6, No. 6 (1996)

On Electroless Plating and Double Sided Buried Contact Silicon Solar Cells

A.U.Ebong, D.S.Kim, S.H.Lee and C.B.Honsberg*

Samsung Advanced Institute of Technology, P.O.Box 111, Suwon 440-600, Korea
**Center for Photovoltaic Devices and Systems, The University of New South Wales, Sydney 2052, Australia*

Abstract The double sided buried contact (DSBC) silicon solar cell processing requires doping of the rear and front grooves with boron and phosphorus respectively. The successful electroless plating of these grooves with the appropriate metals have been found to depend on the boron conditions for the rear fingers. However, an increased understanding of electroless plating has removed this restriction. Thus the DSBC cells using different boron conditions can be electrolessly plated with ease. This paper presents the recent work done on metallizing the double sided buried contact silicon solar cells with heavily doped boron grooves. The cells results indicate that, the heavier the boron grooves, the poorer the cell performance because of the probable higher metal contact recombination associated with boron grooves.

1. Introduction

The buried contact solar cell(BCSC) was designed specifically to conform with low cost, mass production and high efficiency while avoiding many of the usual resistive and shading losses for the metallization. The design specification can only be realized by batch processing of cells and the electroless plating is quite suitable. The electroless nickel and copper plating solutions commercially available, were originally, developed for printed circuit boards. The recommended reaction rates are 2-2.5 microns in 30 minutes for high speed bath and 2-2.5 microns in 15 minutes for double speed bath[1].

For solar cell applications, especially the laser grooved buried contact solar cells, a slower plating rate is required so that the grooves (20μm wide and > 30μm deep) can be filled uniformly with metal. This requires some modifications, especially, the plating temperature which affects the plating speed logarithmically. The plating rate can also be controlled by adding some stabilizer to the plating solution. For the single sided buried contact solar cells, the modified metallization scheme has worked out very well because of the larger plating surface. However, the double sided buried contact cells, because of the smaller plating area and the two different grooves type on front and rear, is more difficult to plate. This requires exploration of conditions that will enable the simultaneous plating of both set of grooves using the commercially available solution.

This paper therefore presents some processing parameters that influence plating and results of double sided cells that have been plated for the first time due to an increased understanding of metallization process. This paper, however, does not cover the effect of plating on the electrical output parameters of the fabricated cells.

2. Buried Contact Solar Cells

The buried contact cell can be classified as single or double sided. The single sided(fig. 1) consists of lightly diffused emitter, front fin-

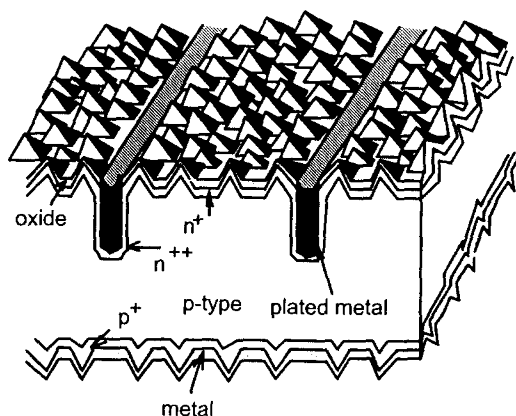


Fig. 1. A schematic diagram of the single sided buried contact solar cell.

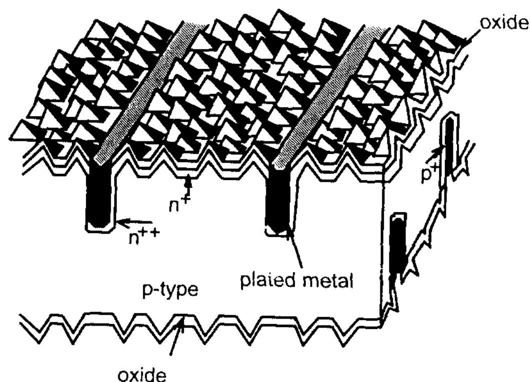


Fig. 2. A schematic diagram of the double sided buried contact solar cell.

gers heavily doped with phosphorus underneath, and thin oxide(seca 1000 angstrom) for anti-reflection coating on the front and rear totally covered with alloyed aluminum. The single sided buried contact(SSBC) cells are capable of giving good electrical performance provided they are fabricated on low resistivity substrates. The higher resistivity substrates are limited to lower open circuit voltages, low fill factors and low conversion energy efficiencies for SSBC cells[2]. This limitation is due to the rear aluminum alloyed contact region which gives rise to high surface recombination velocity at rear surface of the device. The rear aluminum alloyed region contributes a major component to the total device dark saturation current density which determines the open-circuit voltage of the cell. This limitation can be overcome by redesigning the rear of the cell and hence, the double sided buried contact (DSBC) cells[3].

The DSBC cell (Fig. 2) on the other hand consists of lightly doped emitter and rear floating junction, buried contacts on both front and rear heavily doped underneath, and high quality oxides on both sides of the cell. The DSBC cell is simpler and lower in cost than the SSBC cells because the lengthy sintering step for the SSBC cell is eliminated. The elimination of the vacuum evaporator, which is often used for aluminum deposition is expected to significantly reduce the cost of production. It is capable of giving higher open circuit voltages and hence the efficiency than the SSBC cells. It does not depend on substrate resistivity for its performance[4]. It is therefore suitable for a wider range of substrate resistivities than single sided structure whose poor rear surface gives a bias towards lower substrate resistivities for improved performance.

The DSBC cells fabricated before now could only be metallized with certainty if the boron condition is of medium type (see section 4). This has led to energy conversion efficiency of greater than 19% as presented in Table 2. The low fill factor for this cell was attributed to the rear boron grooves effect and the rear floating junction. That is to say, the boron grooves contributes a major component to the dark saturation current of the cell which causes a reduction in the device fill factor. It was suspected that, the boron groove diffusion does not compensate for the rear floating junction of this structure and the low fill factor effect therefore emanate from this non-compensated region. The very heavy boron condition was therefore desirable to completely dispel this suspicion of rear groove effects(that is the non-compensated effect). This condition of rear groove boron diffusion until now was very difficult to plate. However in this work, the

Table 1. The elecrical output parameters of DSBC cells with heavily diffused boron grooves. Cells were fabricated on p-type, Float Zoned, 1 ohm-cm resistivity substrate for $12cm^2$ area.

Cell Id	V_{OC}(mV)	J_{SC}(mA/cm^2)	Fill Factor(%)	Effciency(%)	Ideality factor
AE2-01	639	34.5	78.9	17.4	1.10
AE2-02	631	34.5	77.0	17.1	1.14

Table 2. The elecrical output parameters of DSBC cells with medium diffused boron grooves. Cells were fabricated on p-type, Float Zoned, 1 ohm-cm resistivity substrate for $12cm^2$ area.

Cell Id	V_{OC}(mV)	J_{SC}(mA/cm^2)	Fill Factor(%)	Effciency(%)	Ideality factor
106-1	672	38.1	76	19.5	1.25
108-1	670	38.2	76	19.5	1.30

heaviest boron condition ever used for this structure has been successfully plated and the electrical parameters of such cells are compared with the medium boron condition.

3. Processing sequence of DSBC cells

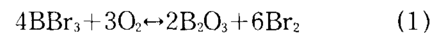
The processing dequence of DSBC cell includes

Wafer texturing
Wafer cleaning
Emitter formation/Oxidation
Rear grooving/Cleaning
Heavy boron groove diffusion/Masking oxide growth
Front grooving/Cleaning
Heavy phosphours groove diffusion
Metallization(Nickel/nickel sinter/copper)
Oxide thinning
Testing

All the processing steps outlined above are very important for good and reproducible results but since the present work concentrates on the boron conditions and metallization, only these two steps would be addressed.

4. Boron Deposition in Silicon

The deposition of boron in silicon is an oxidation diffusion process. It consists of a preliminary reaction of boron bribromide (BBr_3) with O_2 which results in the chemical deposition of boric oxide on the silicon wafers[5]

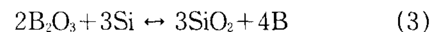


$$4BBr_3+3O_2 \leftrightarrow 2B_2O_3+6Br_2 \quad (1)$$

an interface reaction of oxygen with silicon to form silicon dioxide as well as some interstital silicon[6]

$$Si+O_2 \rightarrow SiO_2 \quad (2)$$

a reaction of boric oxide with silicon to produce silicon dioxide and boron atoms



$$2B_2O_3+3Si \leftrightarrow 3SiO_2+4B \quad (3)$$

and apossible etch of silicon by bromine

$$Si+2Br_2 \rightarrow SiBr_4 \quad (4)$$

Boric oxide is a liquid at normal deposition temperature and mixes readily with the silicon dioxide on the silicon surface to form a boron-silicate glass(BSG). Boron atoms deposited would diffuse into silicon or form a boron-rich surface layer (BRSL). This BRSL is insoluble in buffered hydrofluoric acid (BHF-mixture of ammonium fluoride and hydrofluoric acid (BMF-mixture of ammonium fluoride and

hydrofluric acid in the ratio of 1 : 15) and grows at the interface between BSG and silicon[7].

Rear Boron Groove Diffusion

In this work, BBr_3 liquid source was used. Deposition processes were carried out at 900℃ while the liquid BBr_3 source was kept at 16℃ which corresponds to a partial pressure of 42 mmHg. High purity nitrogen was bubbled through the liquid and mixed with the main carrier consisting of nitrogen and oxygen. This deposition temperature was chosen because of the low oxidation rate and large deposition of B_2O_3 as its pressure increases greatly with temperature. Thus the BSG consists largely of B_2O_3 which may easily dissolve in water. This was applicable to DSBC cell processing as the grooves must be free of oxide while the non-groove areas should be covered with silicon dioxide(masking oxide) during metallization step.

The deposition cycle consisted of a 10 minutes preheating (in N_2 and O_2 ambient at deposition temperature), 20 minutes deposition (BBr_3 plus N_2 and O_2 followed by drive-in at 1070℃ for 90 minutes. The gas flow rates were as follows : N_2 (3.9-3.93 l/min), O_2(78.5-100 ml/min) and N_2+BBr_3(3.93. ml/min). At any given time, the gas flow rate was kept constant (4.05 l/min) by adjusting the main nitrogen flow.

Using different gas compositions three boron diffusion conditions were identified as light, medium and heavy. And the corresponding sheet resistivities were measured (using the four point probe technique) as 300-336$\Omega/\square$, 45-72$\Omega/\square$ and 20-40 $\Omega/\square$ respecitively. Both deposition time/temperature and drive-in time/temperature were kept constant throughout the experiments. The amount of boron diffused into the grooves was controlled by the total oxygen content in the furnace during the diffusion process. For the case of medium boron diffusion condition the gas flow rate were, O_2 88.5ml/min, N_2 3.92ml/min and BBr_3 39.3ml/min. From this data, the light and heavy boron conditions were adjusted. The higher the oxygen content, the lower the amount of boron deposited and vice versa.

The boron diffusion step is a very critical step for DSBC cell sequence. This step is the major difference between the two structures (SSBC and DSBC). This single step influences the end result of the device. If boron is too light (300 ohm/square), the rear floating junction will dominate and often result in badly shunted cells. This effect comes about as a result of the less than optimum oxide to mask the rear groves against the subsequent phosphorus heavy groove diffusion. Thus during the phosphorus front grooves diffusion, the rear grooves would have phosphorus diffused into it.

A medium boron (45-72 ohm/square) is often found to be "just enough" to provide enough masking oxide for the subsequent heavy phosphorus front groove diffusion. This condition is also very easy to deglaze and plate.

Whereas for too heavy boron(20-40 ohm/square), it is very difficult to deglaze and metallize the grooves. This is because the oxide thickness, using the same processing condition, would be thicker than optimum (about 250 nm). However, the increased experience in the processing of DSBC cells and electroless plating in particular provided the solution to this problem.

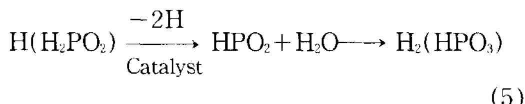
5. Electroless plating of DSBC

Metallization of the DSBC involves the simultaneous plating of metal on the oxide free surfaces within the n^{++} and p^{--} grooves by electroless chemical deposition. The metals are nickel, copper and silver. The starting metal is normally nickel because nickel silicide provides a barrier to the diffusion of copper into silicon. The theoretical understanding of the various electroless plating is important in getting control over the metallization of DSBC cells.

Theory of Electroless Nickel Plating

Nickel plating process is based on catalytic reduction of Ni ions in the presence of hypo-phosphite ions. The hypo-phosphite anions in aquenous medium is oxidized to the phosphite ion with evolution of H, the rate being a function of temperature and hypo-phosphite concentration[8]. This oxidation takes place simultaneously(homogeneous reaction) in alkaline solution at elevated temperature, while, under neutral or moderately acid conditions, the pressence of a catalytic metal belonging to Group VIII of the periodic system, particularly Pd or Ni, is required (catalytic homogeneous reaction).

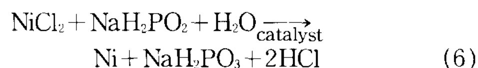
On the basis of organic analogies, electroless nickel plating is assumed to be a catalytic dehydrogenation of the hypo-phosphite molecule according to the equation;



$$H(H_2PO_2) \xrightarrow[\text{Catalyst}]{-2H} HPO_2 + H_2O \longrightarrow H_2(HPO_3) \quad (5)$$

Hypophosphorous acid — Metaphosphorous acid — Orthophosphorous acid

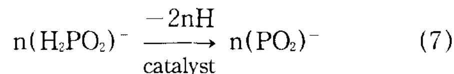
If the metal cation present in the neutral or slightly acid hypo-phosphite solution is that of a catalytic metal such as Ni, and a catalytic solid surface is immersed simultaneously, deposition will be limited to the said surface and will continue until the solution is depleted of hypo-phosphite ion or the metallic cation. The net equation is;



$$NiCl_2 + NaH_2PO_2 + H_2O \xrightarrow[\text{catalyst}]{} Ni + NaH_2PO_3 + 2HCl \quad (6)$$

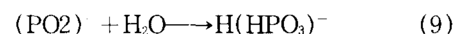
The reduction of Ni ions appears to be caused by atomic (nascent) H adsorbed as a condensed layer on the catalytic surface. Concurrently, there is a secondary reaction among the hypophosphite (and probably the phosphite) ions, atomic H, and Ni cations, resulting in the formation of Ni phosphide (possibly with a phosphonium salt as intermediate compound).

The basic expressions can be given by the following equations:

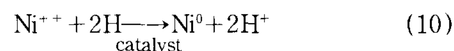


$$n(H_2PO_2)^- \xrightarrow[\text{catalyst}]{-2nH} n(PO_2)^- \quad (7)$$

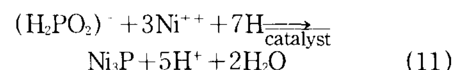
$$2H^+ \longrightarrow H_2 \quad (8)$$



$$(PO2)^- + H_2O \longrightarrow H(HPO_3)^- \quad (9)$$



$$Ni^{++} + 2H \xrightarrow[\text{catalyst}]{} Ni^0 + 2H^+ \quad (10)$$



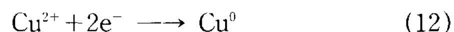
$$(H_2PO_2)^- + 3Ni^{++} + 7H \xrightarrow[\text{catalyst}]{} Ni_3P + 5H^+ + 2H_2O \quad (11)$$

From the catalytic surface of the solid, a stream of H bubbles escapes, and deposition of a high Ni-low P (3-7% phosphorus by weight) alloy takes place. This alloy is itself a catalyst, so that the coating thickness will grow constantly for a certain time period, which is limited by the pH decrease and instantaneous ion concentration. Notably, the pH of the bath drops as the reaction proceeds.

Theory of Electroless Copper Plating

The reactions during copper plating are as follows;

Copper is dissolved as Cu^{2+} and has to be reduced to Cu^0 for the deposition onto the Ni surface:

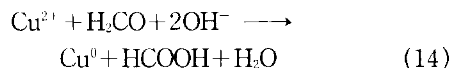


$$Cu^{2+} + 2e^- \longrightarrow Cu^0 \quad (12)$$

As for the redection reaction OH^--ions are required and only in alkaline medium

$$H_2Co + 2OH^- \longrightarrow HCOOH + H_2O + 2e^- \quad (13)$$

And the total reaction is

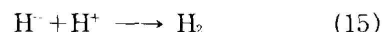


$$Cu^{2+} + H_2CO + 2OH^- \longrightarrow Cu^0 + HCOOH + H_2O \quad (14)$$

In the electroless copper plating solution, copper, sodium hydroxide, formaldehyde, ethylene–diamine derivative and potassium cyanide are involved. The ethylene–diamine derivative and potassium cyanide are important for plating kinetic and selectivity. Both form together with Cu^{2+} ions complexes in aqueous solutions. The ethylene diamine derivative forms square complexes in aqueous solutions. This type of square complexes is necessary to start the deposition of Cu onto the Ni surface. Due to the geometry of this complex an electron transfer from Ni to Cu is possible to form Ni–Cu bond which is the first step of the Cu plating. In contrast to that cyanide–ions form also complexes with Cu–ions which are tetrahedral. Due to the tetrahedral geometry of this complex, no plating occurs, when Cu is fixed by cyanide. As the cyanide complex is stronger than the ethylene–di–amine complex, plating can be stopped by the addition of cyanides.

Following the theory of electroless nickel plating, it would be very easy to plate the DSBC cells with nickel once the surface of the doped semiconductor is free from oxides. However, the type of semiconductor surface determines the ease with which the plating proceeds. In most cases, it is very easy to plate the n–type surfaces than the p–type surfaces[9]. This is because of the presence of the complexing agent such as ethylene di–amine tetra–acetate in most commercially available electroless nickel plating bath. For other semiconductor divices, the use of the activator and sensitizer are very common to enhance the plating of both surfaces. The activator and sensitizer are not suitable for solar cells because they enhance plating on oxides which supposed to be free of metal.

The simultaneous plating of the DSBC n^{++} and p^{++} grooves can sometimes be very difficult, especially with the use of the commercially supplied nickel plating solution, even though the surfaces are free from oxides. Quite unlike the in–house nickel solution[9] which will either plate on both sides or never plate, the commercially supplied solution can plate either front or rear grooves only. This observation could be due to one of the side reactions occurring in the nickel plating bath which is given by the equation[10].



$$H^{-} + H^{+} \longrightarrow H_2 \qquad (15)$$

That is the hydride ions reacting with the hydrogen ions to form hydrogen gas. This reaction reduces the efficiency of the hypo–phosphite utilization which may lead to the non–plating of either grooves. This problem can be overcome with continuous addition of ammonium hydroxide to the plating solution to keep its pH at$>$10 and the temperature maintained at 97℃. This was true for all conditions of boron.

Once nickel has been plated to a surface, the surface should be active enough to initiate copper plating because electroless plating is a catalytic reaction. In most cases this is not true and often lead to cells that are very heavily doped with boron not plating at all. The reason being that, the copper solution could be idle (i. e. no catalytic reaction taking place). The reason for the idle nature of copper solution could be partly due to the cyanide–ions complexing with Cu–ions which is tetrahedral and has the tendency to inhibit plating. The solution can be activated by inserting either of the following; some scratched bare silicon wafers, aluminum foil, nickel metal or wire into the solution. An active copper plating solution is always indicated by white foams on the surface of the solution, otherwise, an aluminum foil can be observed to plate almost immediately in such solution. Once both the copper solution and the nickel surfaces are active the plating will proceed immediately.

Therefore for an ensuring plating of all nickel plated surfaces, before the wafers are immersed in the solution, bubbles on the wall of the container should be observed, which indi-

cates that the solution is active. The bubbles that are observed represent the hydrogen generation which initiates the plating. Further study is in progress to actually understand the mechanism behind the plating rate of electroless copper plating.

It should be noted that, there hasn't been any adhesion problems because there is normally a sintering step after nickel or copper plating process. The adhesion problems normally manifest in the very high contact resistance which would have led to fill factors lower than the reported values. Also, the ideality factors of the cells would have been in the vicinity of 2.

6. Electrical Performance of DSBC cells

Many batches of DSBC cells with the very heavy boron condition have been fabricated and metallized with the following results summarized in table 1. As a comparison Table 2 presents the electrical performance of some sells utilizing the medium boron condition.

Cells presented on both tables were fabricated on the same textured wafers. the only difference is the boron condition. From the two sets of results, it can be seen that, the heavier the boron the poorer the performance of the cells. This could be due to the heavy boron effect on the minority carrier lifetime of the device. That is, the contribution of the heavy boron grooves to the surface recombination velocity is higher than the case of medium boron condition[11]. A full analysis of the two sets of results, based on the dark current-voltage measurements, is presented elsewhere[12].

7. Conclusion

The metallization of the DSBC grooves by electroless nickel can always be ensured if the temperature of the bath is high (>95℃) and the pH is maintained at above 10. The plating of copper on a nickel surface is possible at all times if both the copper solution and nickel surfaces are active. The copper solution can be activated by the insertion of some scratched bare silicon wafers or an agent which can enhance the generation of hydrogen atom in the solution. This increased understanding of the electroless plating has made it possible to metallize DSBC cells irrespective of the boron condition of the rear grooves.

On the cell electrical output performance, it was observed that, the heavy boron condition cells exhibit lower performance than the medium boron conditions. This could, probably, be due to the poor passivating qualities of boron, so that, the heavier the boron the higher the surface recombination velocity contribution which in turn increases the dark saturation current density of the cell and hence reduces the cells open circuit voltage.

Acknowledgments

The contribution of Y. Tang of the Center for Photovoltaic Devices and Systems at the University of New South Wales, Sydney Australia, is highly appreciated. Also, the support of the Australian Research Council is highly appreciated. Other members of the Solar Cell team are gratefull acknowledged.

References

1. The material safety data sheet for copper and plating solutions.
2. C.M.Chong, "Buried Contact Solar Cells", Ph.D. Thesis, The University of New South Wales, Sydney, Australia(1989).
3. A.U.Ebong, S.Ghozati, F.Yun, Y.H.Tang, M.Taouk, C.B.Honsberg, S.R. Wenham and M.A.Green, "Overcoming the Open Circuit Voltage Limits of Buried Contack silicon Solar Cells", 12th European Conference on PV, Amsterdam, (1994) 1775.
4. A. U. Ebong, "Double Sided Buried Contact Silicon Solar Cells", Ph.D. Thesis, The University of New South Wales, Sydney, Australia, (1994).
5. S.F. Guo and W. S. Chen, "A Model for Boron Deposition in Silicon Using a BBR_3",

J. Electrochem. Soc., vol. 125, no.4 (1978) 609.

8. A. W. Godenstein, W. Rostoker and F. Schossberger "Structure of Chemically Deposited Nickel", J.Electrochemistry, 104, 2, (1957) 104.
9. A. U. Ebong, M. Taouk and S. R. Wenham, "A Low Cost Metallization Scheme for Double Sided Buried Contact Solar Cells", Solar Energy Materials and Solar Cells, 31 (1994) 499.
10. A. U. Ebong and S. K. Adjepong, "Fabrication, Metallization and Characterization of p-n Junction diode", Phys. Education, vol.5, no.2, (1988) 92.
11. J. Snel, "The Doped Si/SiO_2 Interface", Solid State Electronics, vol. 24, (1981) 135-139
12. A. U. Ebong, "Computer Aided Analysis of Double Sided Buried Contact Silicon Solar Cells", in preparation (1995).