SELF-DOPING CONTACTS AND ASSOCIATED SILICON SOLAR CELL STRUCTURES

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ABSTRACT: Contacts to <111> Si which are self-doping and self-aligning were investigated. Such contacts are applicable both to conventional cell structures as selective emitters and to more demanding structures such as interdigitated back contact cells. Emphasis was placed on alloyed contacts of Al for providing a self-doping p-type contact and of Ag-Sb for a self-doping n-type contact. Alloying at 900°C of 1.1% (wt.) Sb in Ag doped Si to a value of 2×10^{18} Sb/cm^3, suggesting a 5% (wt.) Sb is needed for ohmic contact. An Al alloy p-n junction was found to be suitable for a solar cell if placed at the back of the cell, with 13.2% efficiency and good IQE demonstrated for a fully screen-printed dendritic web cell. A prototype interdigitated back contact cell was fabricated by screen printing (Al and Ag) with tight alignment (100 μm lines and spaces) on a dendritic web substrate with an efficiency of 10.4%.
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1. INTRODUCTION

An ideal contact material is one which supplies dopant to the silicon immediately beneath it (self-doping), has a high electrical conductivity, makes a mechanically strong bond to the silicon, and does not degrade the electrical quality of the silicon. The required surface concentration for the dopant is $\geq 1 \times 10^{17}$ cm^{-3} for p-type and $\geq 1 \times 10^{19}$ cm^{-3} for n-type. The purpose of this work is to utilize aluminum, widely employed as a contact to p-type silicon, to create an alloy junction in an n-type substrate, and to explore a combination of materials and processes for creating analogous self-doping contacts to n-type silicon. Antimony as the n-type dopant and silver as the primary contact metal appear to satisfy the basic requirements. The silver-silicon phase diagram is similar to the aluminum-silicon phase diagram in that both metals form a eutectic with silicon, at 830°C for silver and 577°C for aluminum. Unlike aluminum, silver is not a dopant, so antimony is added because of its high solubility in silicon, its low cost, and the fact that an alloy of antimony and silver exists as a single, uniform phase for low antimony concentrations (< 6% by weight). The approach is to characterize both the Al-Si and the Ag-Sb-Si material systems using controlled deposition (evaporation and sputtering) and alloying (RTP) methods first, and then to translate the results to the more production-worthy processes of screen printing and belt furnace alloying. Such a contact system benefits conventional cell structures by reducing the need for heavy emitter doping, thereby improving short wavelength response and the effectiveness of surface passivation. Supplying dopant with the contact material is also advantageous to back contact cell structures in that separate doping steps can be entirely eliminated, resulting in a simpler and less costly process.

2. EXPERIMENTAL RESULTS

2.1 Al and Ag-Sb Contacts

Pure Al was evaporated and Ag-Sb (1.1% wt.) was sputtered onto <111> n-type CZ Si substrates. Alloying was done in an RTP unit at 1000°C for Al and at 900°C for Ag-Sb. Cross-sectional samples were prepared and etched to clearly reveal a p$^+$ region for Al and an n$^+$ region for Ag-Sb with depths consistent with the respective phase diagrams.

Figure 1 shows a cross-sectional view of an aluminum alloy junction diode with the resultant self-aligned contact in place. The n-type CZ Si substrate had a <111> orientation, as did all substrates in this work, because these results are to be applied to dendritic web silicon crystals where the surface has a <111> orientation. It appears that the <111> surface leads to a planar p$^+$n junction, without the spiking sometimes observed for a <100> surface. The Al-Si contact boundary is within the p$^+$ region for the samples examined so that shorting between the p$^+$ alloyed region and the n substrate via the Al-Si contact does not seem to be a problem. Tilting of the interface between the contact and the p$^+$ region is probably related to the kinetics of the liquid phase epitaxial regrowth of the p$^+$ region upon cooling. Because the p$^+$ region is generally deep (3 - 10 μm), it is not suitable as an emitter on the illuminated surface for a conventional cell, but the depth is not a concern if such a p$^+$ emitter is at the unilluminated surface of a back contact cell. Of course, alloyed aluminum can make a good contact to a p-type emitter in a conventional cell provided the front emitter is formed independently, e.g., by a boron diffusion.

Figure 2 shows the concept for a self-doping ohmic contact to n-type silicon, by analogy with the action of Al. The result of one implementation of this concept is given in Figure 3 in which the starting metal is an alloy of Ag and Sb which was sputtered onto <111> n-type CZ Si. Electron probe microanalysis gave the composition of the metal before alloying as 1.1% Sb by weight, with the balance being Ag. The metal alloyed with the Si at 900°C in an RTP unit, as evidenced by the crystallographic features of the interaction, and etching showed that the desired structure of Figure 2b was obtained. Wetting of the Si by the Ag-Sb alloy was not uniform, however, as the metal first melted and formed molten islands before alloying with the Si. Follow-on work with a screen-printed paste containing Ag and Sb particles did not "ball up" upon heating as the sputtered metal did.

The self-aligned contact metal was found to have a resistivity of 30 μΩ-cm for Al and 7 μΩ-cm for Ag-Sb. Specific contact resistance was below the detection limit of 5 mΩ-cm^2 for Al. A SIMS profile for a Ag-Sb sample indicated an Sb concentration of 8×10^{18} cm^{-3} at the silicon surface, decreasing rapidly to 2×10^{18} cm^{-3} where it remained nearly constant to the n^+n junction depth of 3.2 μm. A screen-printing paste was then formulated with 5% Sb particles and 95% Ag particles by weight. Contact resistance test patterns were printed and fired in a radiantly heated belt furnace at 900°C. Initial results gave 15 mΩ-cm^2 for contacts to a 75 Ω/□ phosphorus diffused layer and 68 mΩ-cm^2 to a > 700 Ω/□ diffused layer. It was also found that Al paste and Ag-Sb paste could be co-fired and maintain good contact resistance.

2.2 Evaluation of Aluminum Alloy p-n Junction

Aluminum is widely used in the photovoltaic industry to form a back surface field resulting from a high-low junction formed with a p-type substrate. The quality of an aluminum alloy p-n junction was of interest for possible application as a back junction, as in an interdigitated back contact structure. Toward that end, a structure was fabricated by screen-printing of Al and Ag on the back and front, respectively, of n-type (20 Ω-cm) dendritic web silicon substrates. Al was alloyed in an RTP unit in the presence of oxygen for additional surface passivation, while Ag was fired in a radiantly-heated belt furnace. Cells up to 13.2% (4 cm^2 area) were produced (J_{sc} of 31.3 mA/cm^2, V_{oc} of 599 mV, FF of 0.706), indicating a p-n junction suitable for solar cells. Internal quantum efficiency (IQE) was quite good, suggesting a base lifetime in excess of 75 μs.

2.3 Fabrication of Prototype Screen-Printed IBC Web Cell

Figure 4 shows one solar cell structure to which these concepts are being applied. It is an interdigitated back contact cell in which both positive and negative contacts are on the unilluminated side, thereby reducing shadowing losses to zero. With an n-type substrate, the p-n junction is formed by Al alloying while the contact to the substrate is by Ag-Sb. No dopants other than those which are already contained within the metal contacts are required to form the essential features of this structure, provided a high quality surface passivation can be achieved. The structure of Figure 4 does include an n^+ diffusion on the front surface to relax the demands placed on the SiO_2 surface passivation. If Ag-Ga can be used instead of Al, the p-n junction (Ag-Ga), the ohmic contact to the substrate (Ag-Sb), and the surface passivation (SiO_2) could all be accomplished in a single belt furnace processing step, with a fully solderable contact system resulting.

Part of the structure of Figure 4 has been realized in practice. A prototype interdigitated back contact (IBC) cell was fabricated using an n-type 8 Ω-cm dendritic web silicon substrate 114 μm thick. Aluminum gridlines (1000 μm wide) and bus bar were screen printed and alloyed in a belt furnace. Narrow Ag (not Ag-Sb) gridlines (100 μm wide) were then screen printed in an interdigitated fashion with the required alignment tolerances (100 μm gap) and fired in a belt furnace, as shown in Figure 5. The doping required to promote ohmic contact of Ag to Si was done in a separate step. This doped layer had to be removed between the Al and the Ag contacts to eliminate shunting. After applying a TiO_2 AR coating, the parameters for the 2.5 cm wide × 1.0 cm long cell are as given in Figure 6, with an efficiency of 10.4%. The low fill factor is expected to improve when Ag-Sb is used in place of Ag. Additional work, including surface passivation and forming gas anneal, is required. A cell efficiency of 15% is projected, as estimated using PC1D for a 100 μm thick web silicon substrate having 300 μm diffusion length.

3. CONCLUSIONS

From this work, the following conclusions can be drawn:

a. 5% (weight) Sb in Ag is needed to achieve ohmic contact to n-type silicon (1×10^{19} cm^{-3} required), given that 1.1% (weight) Sb in Ag produced an n^+ region doped to 2×10^{18} Sb/cm^3 by RTP alloying at 900°C for 2 minutes;
b. Al alloy p-n junctions are smooth (no spiking) and self-aligned on <111> Si;
c. An Al alloy p-n junction is suitable for a solar cell if placed at the back of the cell, with 13.2% efficiency and good IQE demonstrated for a fully screen-printed dendritic web cell (100 μm thick, 20 Ω-cm base resistivity);
d. An interdigitated back contact cell can be realized by screen printing (Al and Ag) with tight tolerances (100 μm lines and spaces) on a dendritic web silicon substrate, with a prototype cell exhibiting 10.4% efficiency.

4. ACKNOWLEDGMENTS

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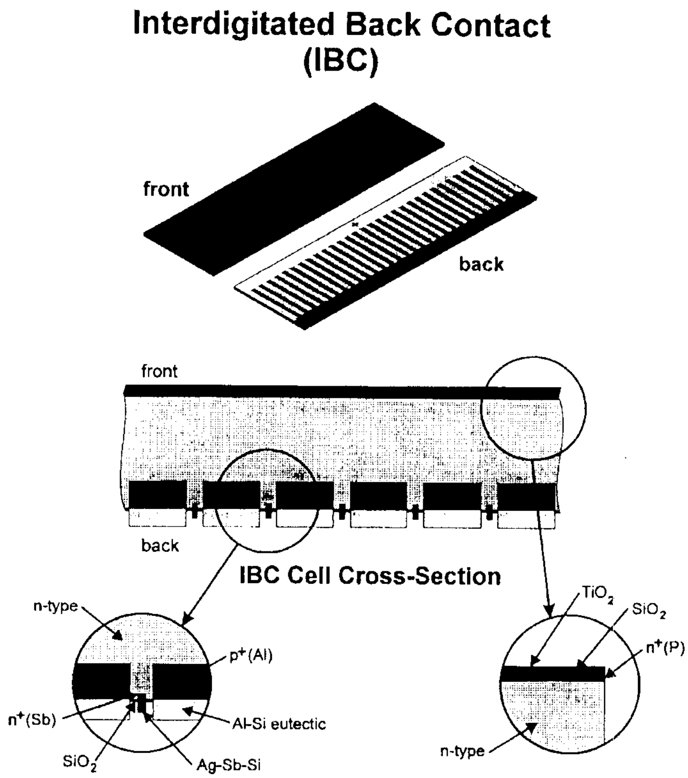


Figure 4: Schematic diagram of target IBC cell structure with Al alloy junction (Al-Si eutectic contact self-aligned with p^+n) and self-doping Ag-Sb negative contact (Ag-Sb-Si contact self-aligned with n^+n).

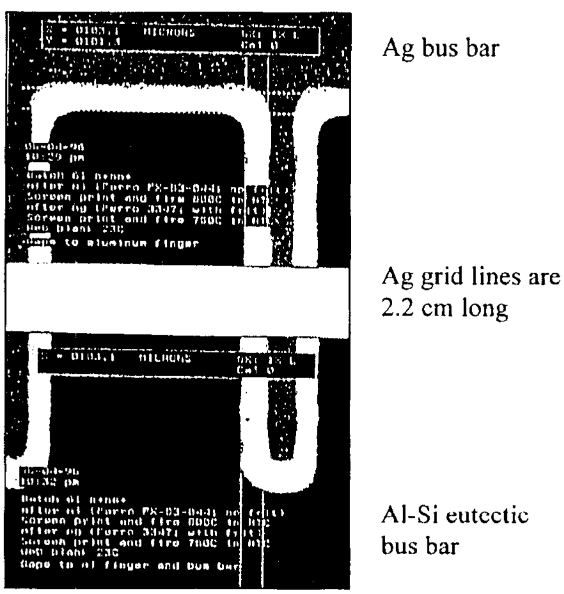


Figure 5: Screen-printed IBC structure after alloying Al and firing Ag showing 100 μm wide Ag lines interdigitated with 1000 μm Al-Si eutectic lines.

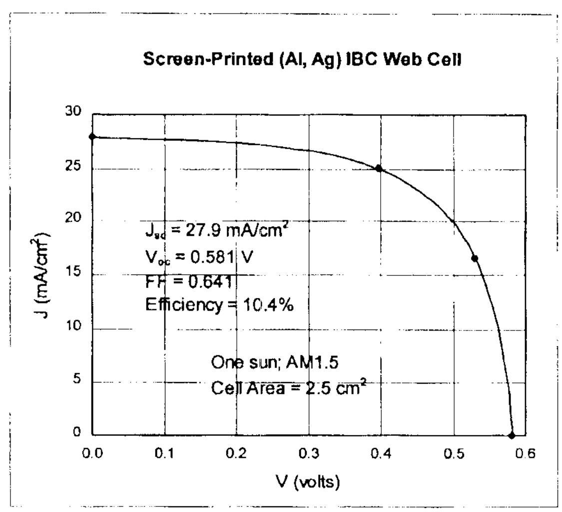
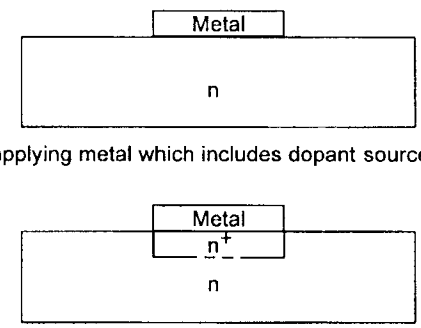


Figure 6: Illuminated I-V curve for prototype IBC cell fabricated on a dendritic web silicon substrate with screen-printed Al alloyed in a belt furnace to form p-n junction and screen-printed Ag fired in a belt furnace for negative contact.

Figure 1: SEM cross-sectional view of Al alloy junction after etching to reveal Al-Si eutectic contact self-aligned with Al-doped p^+ Si on <111> n-type substrate. The Si etch dissolved the silicon-rich phase of the eutectic (rod-shaped channels) and showed a planar bottom to the p^+n junction.



a) After applying metal which includes dopant source, e.g., Ag-Sb

b) After alloying with silicon to produce n^+ beneath the metal only

Figure 2: Schematic view of desired action for self-doping negative contact, in analogy with aluminum forming a self-doping positive contact.

Figure 3: Optical cross-sectional view of Ag-Sb metal on <111> n-type silicon after alloying and etching to show the Ag-Sb-Si contact self-aligned to n^+ Si. Note the planar border between n^+ and n (as in Fig. 2). Thickness of the metal dot is 15 µm.