

# Thermal stability of titanium nitride for shallow junction solar cell contacts

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To demonstrate the thermal stability of titanium nitride as a high-temperature diffusion barrier, the TiN-Ti-Ag metallization scheme has been tested on shallow-junction ( $\sim 2000 \text{ \AA}$ ) Si solar cells. Electrical measurements on reference samples with the Ti-Ag metallization scheme show serious degradation after a  $600^\circ\text{C}$ , 10-min annealing. With the TiN-Ti-Ag scheme, no degradation of cell performance is observed after the same heat treatment if the TiN layer is  $\geq 1700 \text{ \AA}$ . The glass encapsulation of cells by electrostatic bonding requires such a heat treatment.

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Reliable metallic contacts to solar cells have been a subject of interest to the photovoltaic industry. Frequently, the failure or degradation of cell performance is caused by the deterioration of electrical contacts near the  $p$ - $n$  junction during processing steps involving high-temperature thermal treatments. For example, modern packaging processes of solar cells intended for outer-space usage may require an electrostatic bonding step to replace the adhesive presently used to attach thin glass covers to the cell. These covers are about  $150 \mu\text{m}$  thick and protect the cell from damage by energetic particles (primarily protons in the 100-keV range) and also increase the emissivity of the cell in the infrared, thereby reducing the operating temperature of the cell. In the electrostatic bonding process, the metallization scheme is subjected to heat treatment of  $600^\circ\text{C}$  for 10 min. At such elevated temperatures, atomic interdiffusion takes place across the metal-semiconductor interface and the presence of metallic impurities near the  $p$ - $n$  junction can degrade the photovoltaic conversion mechanisms by forming recombination centers. In some severe cases, penetration of the metal through the  $p$ - $n$  junction can even short out the junction completely. These problems are particularly pertinent to shallow-junction solar cells ( $\sim 2000 \text{ \AA}$ ) which are often preferred for their high current efficiency.

To alleviate the interdiffusion problem, it seems promising to apply the concept of diffusion barriers<sup>1</sup> to solar cell metallization schemes. The idea is to interpose material "X," the diffusion barrier, between layers  $A$  and  $B$ , so that the undesirable thermal diffusion is suppressed while the electrical and mechanical properties of the  $A$ - $X$ - $B$  structure remain unaltered or at least equivalent to the  $A$ - $B$  metal combination. An important aspect of the diffusion barrier concept is to free the designer from various metallurgical constraints. Since the choice of metals is generally dictated by metallurgical and processing considerations, the application of an appropriate diffusion barrier may provide more variety to the selection of materials.

As a choice for the diffusion barrier material, we have

singled out titanium nitride (TiN) because of its low electrical resistivity and high chemical stability. Metallurgical studies on the diffusion barrier properties of TiN have been reported by Wittmer<sup>2</sup> on metal-metal couples and by Cheung *et al.*<sup>3</sup> on metal-silicon systems. Fournier<sup>4</sup> has applied a layer of TiN between Ti and Pt layers in the metallization scheme for insulated-gate field-effect transistors. His results demonstrate that the diffusion of Pt into Ti is blocked effectively during a heat treatment of 30 min at  $450^\circ\text{C}$ . In the Au-Pt-Ti scheme for beam-lead devices, Garceau *et al.*<sup>5</sup> have also reported that the incorporation of a  $100\text{-\AA}$ -thick TiN layer between Ti and Pt can inhibit the formation of the intermetallic TiPt. In the present study, we have demonstrated the thermal stability of TiN as a diffusion barrier up to  $600^\circ\text{C}$  for shallow-junction ( $\sim 2000 \text{ \AA}$ ) Si solar cell contacts.

The  $2 \text{ cm} \times 2 \text{ cm}$   $n^+$ -on- $p$  Si solar cells with a junction depth of  $\sim 2000 \text{ \AA}$  were provided by Applied Solar Energy Corporation. The  $n^+$  layer is phosphorus doped. The boron-doped  $p$ -type substrates ( $\sim 10 \text{ mil}$  thick) are from Czochralski-pulled Si crystals and are coated with  $4 \mu\text{m}$  of Ag as the back contact. In this feasibility study, the special metallization pattern on the cells consists of parallel fingers about  $1 \text{ mm}$  wide and  $\sim 1 \text{ mm}$  apart. Mechanical masking procedures were used to define the patterns during TiN deposition and metal evaporation.

The TiN thin films were prepared in a rf sputtering deposition chamber equipped with  $7.5\text{-cm}$  diameter, planar magnetron sputtering targets (pure Ti). A sputtering rf power of  $1 \text{ kW}$  and nitrogen pressure of  $70 \text{ mT}$  were used for the reactive sputtering of TiN, with typical deposition rates of  $\sim 100 \text{ \AA}$  per minute. Different TiN thicknesses were obtained by varying the deposition times. The electrical resistivity of the TiN layers was on the order of  $500 \mu\Omega \text{ cm}$ . Although lower resistivities can be obtained by higher sputtering powers and lower nitrogen pressures,<sup>6</sup> it has been observed that the adhesion of TiN to silicon is satisfactory only at higher nitrogen pressures. Despite the higher bulk resistivity of TiN (approximately a factor of 4 higher than that of evaporated Ti films), the TiN-Ti-Ag system has an  $I$ - $V$  performance comparable with the Ti-Pd-Ag metalliza-

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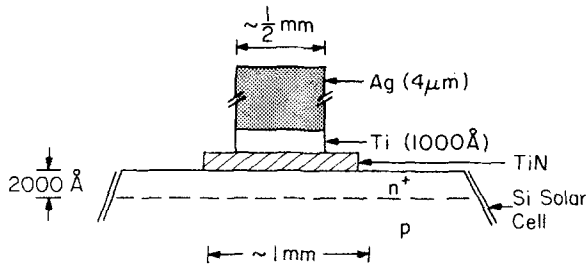


FIG. 1. Schematic of the TiN-Ti-Ag metallization system on a Si solar cell.

tion scheme when tested on the  $n^+$ -on- $p$  solar cells. This is because the effective series resistance  $R_s$  of the cell is dominated by contact resistance across the metal-Si interface and series resistance along the metallic stripes. With a  $4\text{-}\mu\text{m}$ -thick and  $1\text{-cm}$ -long Ag layer as the major electrical conductor, the resistance across the TiN thickness ( $1000\text{--}2000\text{ \AA}$ ) will contribute negligibly to  $R_s$ .

The schematic of the metallization layers is shown in Fig. 1. After the TiN layer deposition ( $500$  to  $2000\text{ \AA}$  in thickness), a thin Ti layer ( $\sim 1000\text{ \AA}$ ) was evaporated on top of TiN in a separate evaporation chamber followed by a  $4\text{-}\mu\text{m}$ -thick Ag layer. The Ti layer was used to improve the adhesion between Ag and TiN. To avoid mask registration problems, the Ti and Ag stripes were made only  $\frac{1}{2}\text{ mm}$  wide so that they would not overlap the edges of the TiN layer.

The  $600\text{ }^\circ\text{C}$  annealing was performed under manufacturing conditions with a flowing nitrogen ambient. No particular attention was paid to the dryness of the nitrogen gas or the presence of oxygen in the annealing ambient. Prior to the  $600\text{ }^\circ\text{C}$ ,  $10\text{-min}$  heat treatment, all the cells were sintered

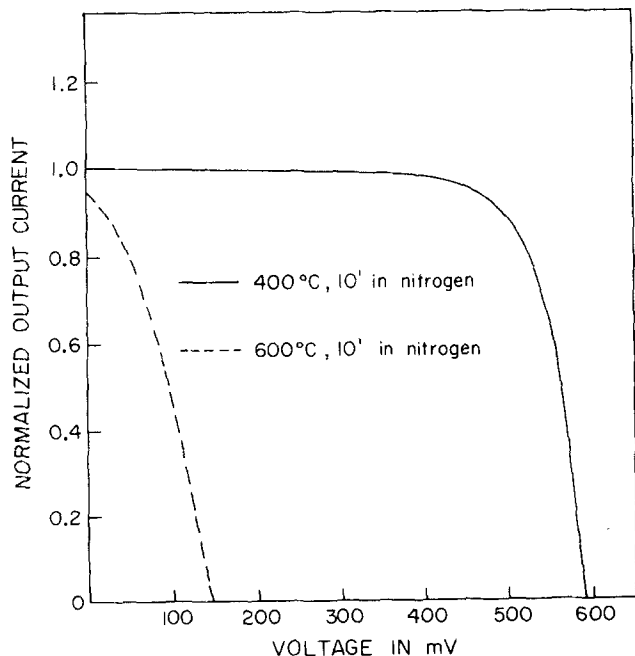


FIG. 2.  $I$ - $V$  characteristic of a shallow-junction ( $\sim 2000\text{ \AA}$ ) Si solar cell with the Ti-Ag metallization scheme under AMO illumination. The solid line denotes the cell's performance after a  $400\text{ }^\circ\text{C}$ ,  $10\text{-min}$  annealing. The dashed line shows the degradation after a  $600\text{ }^\circ\text{C}$ ,  $10\text{-min}$  heat treatment.

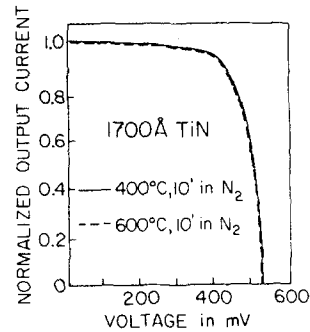


FIG. 3.  $I$ - $V$  characteristic of a shallow-junction ( $\sim 2000\text{ \AA}$ ) Si solar cell with the TiN-Ti-Ag metallization scheme before (solid line) and after (dotted line), a  $400\text{ }^\circ\text{C}$ ,  $10\text{-min}$  annealing. The dashed line represents the cell's performance after a  $600\text{ }^\circ\text{C}$ ,  $10\text{-min}$  annealing. The TiN layer is  $\sim 1700\text{ \AA}$  thick. The  $I$ - $V$  curves are measured with AMO illumination.

at  $400\text{ }^\circ\text{C}$  for  $10\text{ min}$  to minimize the contact resistance between the metallization and Si.

For comparison, reference samples without the TiN layer (i.e., the Ti-Ag metallization scheme) were also prepared and heat treated at  $600\text{ }^\circ\text{C}$  for  $10\text{ min}$ . Results on the  $I$ - $V$  measurements under AMO illumination are shown in Fig. 2. Both  $V_{oc}$  (open circuit voltage),  $I_{sc}$  (short circuit current) and the fill factor are observed to be significantly reduced after the thermal annealing. Following the analysis of Hovel,<sup>7</sup> the results indicate that the shunt resistance  $R_{sh}$  and the series resistance  $R_s$  of the junction and metallization scheme are lowered and raised, respectively. The decrease in  $R_{sh}$  reflects the fact that the  $p$ - $n$  junction can either be contaminated or even short circuited locally by the presence of metallic elements. The intermixing of Si-Ti-Ag can lead to an increase in  $R_s$  because of the increase in the contact resistance with Si and/or the resistivity of the metal films by forming a ternary alloy. This observation is in good agreement with previous diffusion studies that established the thermal instability of the Si-Ti-Ag system at  $600\text{ }^\circ\text{C}$ .<sup>3</sup>

The  $I$ - $V$  characteristic of solar cells with the TiN-Ti-Ag metallization scheme was also measured under AMO illumination before and after the  $600\text{ }^\circ\text{C}$ ,  $10\text{-min}$  annealing cycle. For TiN thicknesses between  $750$  and  $1700\text{ \AA}$ , no degradation of  $V_{oc}$  could be detected, which indicates that  $R_{sh}$  remains constant during the heat treatment. However, the fill factor of the  $I$ - $V$  curves shows a thickness dependence on the TiN layer and decreases with decreasing TiN layers. Beyond a TiN thickness of  $1700\text{ \AA}$ , no change in  $V_{oc}$ ,  $I_{sc}$ , and fill factor can be detected after the  $600\text{ }^\circ\text{C}$  annealing (Fig. 3). Thus, with a sufficiently thick TiN layer, the normal failure mode of Si solar cells after high-temperature heat treatments can be circumvented without sacrifice in the cells' electrical performance.

In summary, we have demonstrated that TiN films can be used as a diffusion barrier for high-temperature processing. In particular, with the TiN-Ti-Ag metallization scheme on shallow-junction ( $\sim 2000\text{ \AA}$ ) Si solar cells, no degradation of cell performance is observed after a  $600\text{ }^\circ\text{C}$ ,  $10\text{-min}$  heat treatment if the TiN layer is  $\geq 1700\text{ \AA}$ . In practice, a  $500\text{-}\text{\AA}$ -thick Pd layer would be sandwiched between the Ti and Ag layers to passivate the electrochemical reaction between Ti and Ag when the cells are exposed to moisture.<sup>8</sup>

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- <sup>1</sup>M-A. Nicolet, *Thin Solid Films* **52**, 415 (1978).
- <sup>2</sup>M. Wittmer, *Appl. Phys. Lett.* **36**, 456 (1980).
- <sup>3</sup>N. W. Cheung, H. von Seefeld, and M-A. Nicolet, in *Proceedings of the Symposium on Thin Film Interfaces and Interactions*, edited by J. E. E. Baglin and J. M. Poate (The Electrochemical Society, Princeton, 1980), Vol. 80-2, p. 323.
- <sup>4</sup>P. R. Fournier, U. S. Patent 3 879 746 (1975).
- <sup>5</sup>W. J. Garceau, P. R. Fournier, and G. K. Herb, *Thin Solid Films* **60**, 237 (1979).
- <sup>6</sup>M. Mäenpää, H. von Seefeld, N. W. Cheung, M-A. Nicolet, and A. G. Cullis, in *Proceeding of the Symposium on Thin Film Interfaces and Interactions*, edited by J. E. E. Baglin and J. M. Poate (The Electrochemical Society, Princeton, 1980), Vol. 80-2, 316.
- <sup>7</sup>H. J. Hovel, *Semiconductors and Semimetals, Vol. II: Solar Cells* (Academic, New York, 1975), p. 78.
- <sup>8</sup>H. Fischer and R. Gereth, *IEEE Trans. Electron Dev.* **ED-10**, 459 (1979).