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Solar Energy Materials & Solar Cells 72 (2002) 231–246

**Solar Energy Materials
& Solar Cells**

www.elsevier.com/locate/solmat

Defect passivation of industrial multicrystalline solar cells based on PECVD silicon nitride

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Abstract

Low surface recombination velocity and significant improvements in bulk quality are key issues for efficiency improvements of solar cells based on a large variety of multicrystalline silicon materials. It has been proven that PECVD silicon nitride layers provide excellent surface and bulk passivation and their deposition processes can be executed with a high throughput as required by the PV industry. The paper discusses the various deposition techniques of PECVD silicon nitride layers and also gives results on material and device properties characterisation. Furthermore the paper focuses on the benefits achieved from the passivation properties of PECVD SiN_x layers on the multi-Si solar cells performance. This paper takes a closer look at the interaction between bulk passivation of multi-Si by PECVD SiN_x and the alloying process when forming an Al-BSF layer. Experiments on state-of-the-art multicrystalline silicon solar cells have shown an enhanced passivation effect if the creation of the alloy and the sintering of a silicon nitride layer (to free hydrogen from its bonds) happen simultaneously. The enhanced passivation is very beneficial for multicrystalline silicon, especially if the defect density is high, but it poses processing problems when considering thin ($<200\text{ }\mu\text{m}$) cells. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solar cells; Multicrystalline silicon; Defects; Hydrogen passivation

1. Introduction

With the current stable growth of the PV shipments of around 30% the total world PV production will reach a GWp level already by the year 2005. Crystalline silicon solar cells constitute more than 85% of the world PV market with a tendency to increase the market share. To follow the production growth, cell manufacturers are

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forced to shift from good quality mono-Si wafers to different types of lower quality polycrystalline substrates: cast multi-Si wafers, ribbons and thin polycrystalline-Si films. All these materials are characterised by large inhomogeneities caused by grain boundaries and intra-grain defects like dislocation, twins and others. These inherent defected regions act as recombination centres of minority carriers.

Due to silicon supply problems, often a low quality feedstock is used, introducing various impurities in an uncontrolled way. Metallic impurities, oxygen and carbon behaving themselves as recombination centres, interact additionally with the crystallographic defects enhancing their recombination properties [1]. It is obvious that such imperfect multicrystalline silicon substrates are characterised by a very low lifetime of minority carriers. A wrongly designed cell processing sequence can increase impurity segregation at the defected regions and consequently increase their recombination activity. Therefore the thermal treatments must often be tuned to the properties of specific multi-Si materials. There are, however, several processing techniques which, when combined in a well thought-out solar cell processing sequence, can drastically improve the starting lifetime. Impurities like oxygen and metallic fast diffusers (Fe, Cu, Ni, Cr) can be efficiently extracted by external gettering occurring during the emitter diffusion from POCl_3 source [2] and/or during the aluminium silicon alloying process commonly used for BSF formation.

Defects, impurities and segregated impurities on extended defects can be passivated by hydrogen [3]. There are several techniques developed for hydrogen passivation of silicon bulk and surfaces. The best known are: annealing in forming gas ambient, H ion implantation, direct and remote plasma hydrogenation and deposition of H-containing silicon nitride layers ($\text{SiN}_x\text{:H}$).

2. Deposition techniques of the $\text{SiN}_x\text{:H}$ layers

The hydrogen containing silicon nitride layers are becoming widely introduced in industrial crystalline silicon solar cell processes thanks to the unique possibility of combining in one processing step an antireflection coating deposition along with surface and bulk passivation [4,5]. Chemical, mechanical, optical and electrical properties of silicon nitride as well as the effectiveness of surface and bulk passivation strongly depend on the selected deposition technique. For solar cell application the most suitable are the deposition processes from the gas phase by means of chemical vapour deposition (CVD) using silane, ammonia and/or nitrogen as the reactant gases. The resulting silicon nitride layers are usually non-stoichiometric and contain up to 40 at% of hydrogen and are usually denoted in the literature as $\text{SiN}_x\text{:H}$. The three basic CVD processes are: atmospheric pressure (APCVD), low pressure (LPCVD) and plasma enhanced (PECVD). APCVD involves reaction of silane and ammonia at atmospheric pressure in the temperature range of 700–900°C. LPCVD involves the reaction of dichlorosilane and ammonia at reduced pressure (~ 0.1 Torr) and temperatures around 750°C. PECVD uses plasma-enhanced reaction of silane and ammonia (or optionally nitrogen) at reduced pressure (~ 1 Torr) and temperatures below 500°C. The PECVD method is of

particular interests for solar cell application. The main advantages of the PECVD method over APCVD and LPCVD are: low processing temperature, higher deposition rate, the possibility to tune the refractive index over a wide range and much larger concentration of hydrogen in the deposited layers. The refractive index of PECVD SiN_x layers can be varied in a range of 1.8 and 2.3 by means of the silane/ammonia ratio. A trade-off has to be found between minimisation of reflection and reduction of energy loss by absorption of short wavelength photons in the $\text{SiN}_x\text{:H}$ layer. The main reason for the strong interests in PECVD $\text{SiN}_x\text{:H}$ stem however not from the antireflection properties but mainly from the fact that there is overwhelmingly strong evidence for the very good surface and bulk passivation properties of the PECVD $\text{SiN}_x\text{:H}$ layers. The appropriate implementation of PECVD $\text{SiN}_x\text{:H}$ into a low-cost multicrystalline silicon solar process leads to comparable surface passivation and bulk passivation to respective dry oxide and prolonged hydrogenation passivation processes. Important pioneering work regarding SiN_x -passivation and its application to silicon solar cells has been conducted during the past decades by J. Hanoka and co-workers [6].

There are two basic different methods of PECVD $\text{SiN}_x\text{:H}$ deposition: direct and remote PECVD. In direct PECVD reactors all processing gasses (silane, ammonia, and nitrogen) are directly injected between the electrodes and excited by an electromagnetic field. The silicon substrates are placed within the plasma. Depending on the generator frequency, one can distinguish a “low frequency” (10–500 kHz), a “high frequency” (13.56 MHz) or a “very high frequency” (30–100 MHz) direct plasma excitation. The excitation frequency influences the effectiveness of the surface and bulk passivation. Heavy ion bombardment present in a low frequency direct plasma produces a surface damage and therefore lower quality silicon surface passivation is achieved than in case of high or very high frequency direct plasma deposited $\text{SiN}_x\text{:H}$ layers [7]. On the other hand it is believed that some surface damage enhances in-diffusion of hydrogen into silicon and helps in bulk passivation [3].

In the remote plasma CVD technique, the plasma excitation takes place outside the deposition chamber usually by means of microwaves, hollow cathode or arc jet. In most cases only ammonia or a nitrogen/hydrogen mixture are excited and directed onto a silicon substrate. Silane is injected downstream directly into the deposition chamber and is mainly dissociated by the atomic hydrogen from the plasma source. The main advantages of the RPECVD $\text{SiN}_x\text{:H}$ are the much higher deposition rate and the absence of silicon surface damage. Important for the solar cell working conditions is that RPCVD and high frequency direct plasma are reported to provide UV stable and excellent surface passivation [7]. The broad overview on silicon nitride surface passivation of crystalline silicon solar cells can be found in [7]. There is however still a question about the extent of bulk passivation from RPECVD deposited SiN_x layers in comparison to Direct PECVD layers.

A great interest from the PV industry in implementation of the PECVD $\text{SiN}_x\text{:H}$ layers in an industrial multi-Si solar cell process triggered the developments of dedicated high throughput deposition systems. There are several commercial systems being currently in the advanced development phase or already introduced on the

market. These systems are based either on direct plasma parallel plate reactor [8], microwave remote plasma [7,9] or very high throughput expanding thermal plasma [10].

In the next chapters the properties of direct plasma PECVD silicon nitride layers combined with a low cost screen printing process is described in detail and analysed.

3. Screen-printed multicrystalline cells with SiN_x -passivation

3.1. Process specifications

The previous paragraphs have introduced the different methods available for deposition of SiN_x -layers including direct PECVD, which is very well suited for application on silicon solar cells. At IMEC's solar cell pilot line extensive process optimisations have been conducted to improve the efficiency of multicrystalline silicon solar cells using the inherent passivation properties of silicon nitride. Experiments have shown that it is very advantageous to apply a heat treatment after silicon nitride deposition to free hydrogen, which is present in the layer at high concentrations, from its bonds to silicon and nitrogen. Consequently hydrogen can diffuse out of the layer into the cell and bind itself to dangling bonds in the defected multicrystalline material (passivation). A comparison of two process sequences, with and without a thermal treatment of the silicon nitride layer, is shown in Fig. 1.

The process with thermal treatment of the silicon nitride layer is referred to as a “firing-through” process since the front cell contacts (Ag) are fired through the nitride layer to make contact with the underlying emitter during this high temperature step. The duration and the temperature profile for this firing step are chosen to achieve a good contact (a high Fill Factor (FF)) between the emitter and the front contact. On state-of-the-art multicrystalline material, improvements of 1% absolute have been

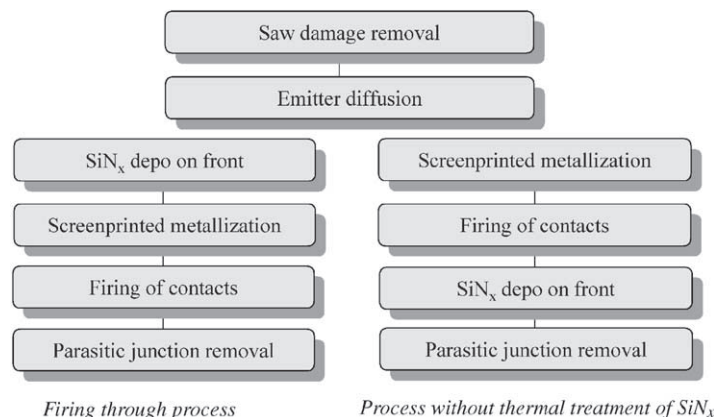


Fig. 1. Process sequence with and without thermal treatment.

obtained with the firing-through process compared to the reference process without thermal treatment of silicon nitride. Internal Quantum Efficiency measurements [11] of these cells have shown a higher response for photons of all wavelengths indicating that the improvement due to the hydrogen passivation reaches far into the bulk of the cell. For the reference process (no thermal treatment), the bulk of the cells is not affected and therefore it can be stated that no bulk passivation occurs if the nitride is not thermally treated.

The effect of the bulk passivation from the firing-through process strongly depends on the material quality. In general it can be stated that the more defected the material, the higher the improvement will be from the firing-through-SiN_x process. This is confirmed by the results of Table 1 that compare firing-through-TiO_x (no bulk passivation) and firing-through-SiN_x processes on material of lower starting quality.

This process, which is straightforward and can easily be implemented in existing production lines, can nevertheless effectively passivate the bulk of multicrystalline cells resulting in an important efficiency improvement. Although the prime purpose of the firing through process is to incorporate a bulk passivation in the process sequence, the newly developed process also brings other advantages specifically related to the use of silicon nitride. Some of these are discussed below.

3.2. Advantages of firing-through SiN_x process

3.2.1. Emitter passivation

The silicon nitride effectively passivates the emitter of silicon solar cells. This has been experimentally verified by making a comparison of cells with and without a dry oxide beneath the silicon nitride layer. The results of both groups are similar for industrial-type emitters on condition that the silicon nitride is thermally treated. If the nitride coating is not thermally treated, damage resulting from the ion bombardment during plasma deposition degrades the surface quality resulting in a J_{0e} that is twice as high (1.3×10^{-12} A/cm² compared to 6.2×10^{-13} A/cm²). With thermal treatment at temperatures above 700°C, this damage is annealed.

3.2.2. Diffusion barrier

Silicon nitride acts as a diffusion barrier during contact firing. This inherent property of nitrides is well known in the microelectronics industry. Likewise the silicon nitride used in our process acts as a diffusion barrier against unwanted impurities. As a consequence, metal spikes deep into the silicon can be avoided

Table 1
Comparison of firing-through-SiN_x and TiO_x processes on defected material

Process	Jsc (mA/cm ²)	Voc (mV)	FF (%)	Eff. (%)
Firing through TiO _x	28.0	585	76.5	12.5
Firing through SiN _x	30.6	600	76.9	14.1

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