Silicon Nitride Layer Deposited at Low Temperature for Multicrystalline Solar Cell Application

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Abstract

Plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN) is a proven technique for obtaining layers that meet the needs of surface passivation and anti-reflection coating. In addition, the deposition process appears to provoke bulk passivation as well due to diffusion of atomic hydrogen. This bulk passivation is an important advantage of PECVD deposition when compared to the conventional CVD techniques. A further advantage of PECVD is that the process takes place at a relatively low temperature of 300℃, keeping the total thermal budget of the cell processing to a minimum. In this work SiN deposition was performed using a horizontal PECVD reactor system consisting of a long horizontal quartz tube that was radiantly heated. Special and long rectangular graphite plates served as both the electrodes to establish the plasma and holders of the wafers. The electrode configuration was designed to provide a uniform plasma environment for each wafer and to ensure the film uniformity. These horizontally oriented graphite electrodes were stacked parallel to one another, side by side, with alternating plates serving as power and ground electrodes for the RF power supply. The plasma was formed in the space between each pair of plates. Also this paper deals with the fabrication of multicrystalline silicon solar cells with PECVD SiN layers combined with high-throughput screen printing and RTP firing. Using this sequence we were able to obtain solar cells with an efficiency of 14% for polished multi crystalline Si wafers of size 125 mm square.

1. Introduction

In recent years, low temperature (less than 350℃) silicon nitride layers have a number of important applications in the flat panel display. They are used extensively for the passivation of devices, i.e., protection of completed devices from a hostile environment, and as a dielectric in thin film transistor (TFT) [1] or surface passivation and anti-reflection coating (ARC) of solar cell [2]. Excellent step coverage, good adhesion to underlying layers and a diffusion barrier to water vapor and sodium ions, make SiN:H ideal for encapsulating devices after the final metallization layer. It also gives particle and scratch protection to devices during mounting operations. Recently many work showed that the optimum surface passivation is observed for stoichiometric SiN films (n~1.9 at 633 nm) [3,4]. Surface passivation plays a crucial role in the fabrication process of high efficiency multi-crystalline silicon (mc-Si) solar cells [5-7]. Plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN) is a proven technique for obtaining layers that meet the needs of surface passivation and anti-reflectioncoating. In addition, the deposition process appears to provoke bulk passivation as well due to diffusion of atomic hydrogen. This bulk passivation is an important advantage of PECVD deposition when compared to the conventional CVD techniques. A further advantage of PECVD is that the process takes place at a relatively low temperature of 300C, keeping the total thermal budget of the cell processing to a minimum. This article demonstrates the optimization of growth conditions of the SiNx:H films grown by Plasma Enhanced Chemical Vapor Deposition (PECVD) using pure nitrogen and a silane/ammonia mixture which can provide good passivation and can act as Anti-reflection coating.

2. Experimental

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 [8,9]. Chemical, mechanical, opticaland 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. PECVD uses plasma enhanced reaction of silane and ammonia or optionally nitrogen at reduced pressure (around 1 Torr) and temperatures below 500℃. 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 [7]. In the present work, SiNx deposition was performed using a horizontal PECVD reactor system consisting of a long horizontal quartz tube that was radiantly heated. Special and long rectangular graphite plates served as both the electrodes to establish the plasma and holders of the wafers. The electrode configuration was designed to provide a uniform plasma environment for each wafer and to ensure the film uniformity. These horizontally oriented graphite electrodes were stacked parallel to one another, side by side, with alternating plates serving as power and ground electrodes for the RF power supply. The plasma was formed in the space between each pair of plates. In a single run, we were able to simultaneously deposit SiN layers over 20 wafers. Also, in the present work, SiN films of different refractive index in the range from 1.9 to 2.3 were prepared by varying the gas ratio between ammonia and silane and the resulting thickness and refractive index of the SiN films prepared by PECVD are characterized by Spectroscopic Ellipsometry (SE) measurements, which is used in the recent past for the non-destructive characterization of solids. The main reason for the strong interests in PECVD SiNx:H stems 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 SiNx:H layers. Also this paper deals with the fabrication of multicrystalline silicon solar cells with optimized PECVD SiNx:H layers combined with high-throughput screen printing and RTP firing.

3. Results and discussion

3.1. Anti-reflection coating

The silicon nitride coating used in the firing-through process has a double aim: it's not only a source of hydrogen (passivation) but also acts as an excellent antireflection coating or ARC [7]. This is an important advantage in comparison with other processes that incorporate bulk passivation (e.g. based on plasma hydrogenation). In that case, a separate step is still needed to deposit an ARC. The purpose of an ARC is to reduce the reflection of incoming light photons by favouring destructive interference of photons impinging and reflecting from the Air/SiNx/Si interface. This effect is mainly influenced by the thickness of the layer and its refractive index. Ideally the refractive index is around 1.9 for the Air/SiNx/Si structure and around 2.3 for the encapsulated condition. Since all cells are finally put into a module, the value of 2.3 is the one that's most important. However this observation makes abstraction from another feature: light absorption. When the extinction coefficient of the deposited layer rises more light will be absorbed in the layer itself. These photons will therefore not contribute to the cell current. Characterizations based on spectroscopic-Ellipsometry have indicated that this effect becomes especially important for short-wavelength light. This effect is directly influenced by the NH_3/SiH_4 ratio during deposition. If more silicon incorporated in the layer (lower NH_3/SiH_4 ratio), the extinction coefficient (and the absorption losses) as well as the refractive index will rise. At higher refractive indices, the reflection losses will be lower but this will be over compensated by the absorption loss (higher extinction coefficient) in the layer itself. Experiments have shown that, for this reason, even for the encapsulated condition, it is favourable to limit the refractive index to values around 2.0. In order to get different refractive index of the SiNx film, we have deposited the films under different ammonia to silane ratio with a fixed RF power of 200 W and the substrate temperature maintained at 300℃. Before SiNx depositionwe have treated the wafers with NH_3 plasma for five minutes. The refractive index and thickness of the films were measured using spectroscopic ellipsometry. With our gas ratio we were able to tune the refractive index from 1.8 to 2.3. The details of the gas ratio and the variation of refractive index with the NH_3/SiH_4 is shown in Fig.1. From the figure we can observe the decrease in the refractive index with the increase in the NH_3/SiH_4 ratio. Also the variation of deposition rate with the NH_3/SiH_4 ratio is depicted in Fig. 2, which shows the decrease in deposition rate of the films with the increase in the NH_3/SiH_4. The low refractive index and lower deposition rate was observed for nitrogen rich samples, but as the Silane quantity increases the refractive index and deposition rate was found to increase, because the samples are Si rich.

Fig. 3 shows the reflection of the bare mc-si wafer and also the reflectance after diffusion and SiNx AR coating, which clearly shows the effectiveness of the SiNx AR coating layer.

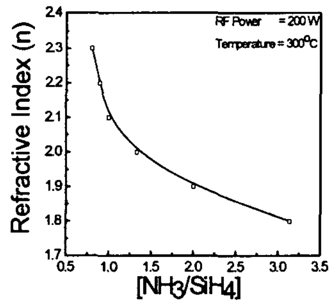

Fig.1. Variation of 'n' with NH_3/SiH_4 ratio.

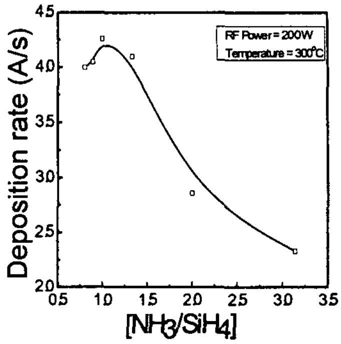

Fig. 2. Variation of deposition rate with gas NH_3/SiH_4 ratio.

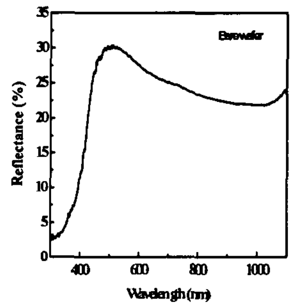

Fig. 3. (a) Diffuse reflectance spectra of the bare deposited mc-Si wafers.

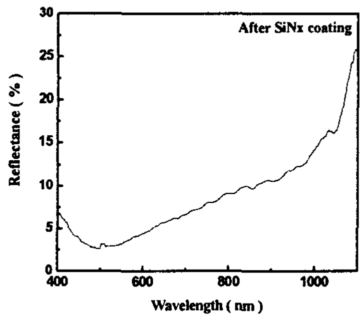

Fig. 3(b) Diffuse reflectance spectra of the SiNx:H deposited mc-Si wafers.

3.2. mc-Silicon solar cell fabrication

We have started with the bare mc-Si of size 125 mm square, the surface of the wafer was acid polished using a solution which contains $HF:HNO_3:CH_3COOH$ in the ratio 1 : 4 : 1. Then the wafers were $POCL_3$ doped using a conventional doping process followed in the industrial process. In the current work, $POCl_3$ doped wafers with a junction depth of about 0.5 m and an emitter sheet resistance of 35 ohm/□ were selected for cell fabrication. The doped wafers were then edge isolated and then SiNx:H antireflection and passivation layer with a refractive index of 1.9 and thickness 700 A was deposited using the optimized deposition conditions mentioned in detail in the previous section. After that we have given the metal contacts using high-throughput screen printing technique with full Al on the back and also Ag front contacts followed by RTP (rapid thermal processing) firing. 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. Using this sequence we were able to obtain solar cells with an efficiency of 14% for multi crystalline polished Si wafers of size 125 mm square. The light illuminated current-voltage characteristic of the prepared solar cell is shown in Fig. 4. The mean cell efficiency, fill factor and Voc for the cells prepared in the present study were found to be 14 %, 0.74 and 0.601 V respectively.

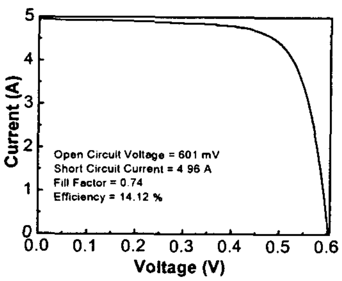

Fig. 4. LIV characteristics of the fabricated mc-silicon solar cell

4. Conclusions

SiNx films have been deposited using pure nitrogen and silane/ammonia mixture in a PECVD system. High quality silicon nitride is obtained with a RF power of 200W with the substrates maintained at a temperature of 300 ℃. Variation of refractive index and deposition rate were studied as a function of ammonia and silane gas ratio. With this process we were able to fix the refractive index between 1.8 and 2.3. The low refractive index and lower deposition rate was observed for nitrogen rich samples and a reverse case was observed for Si rich films. At higher refractive indices, the reflection losses will be lower but this will be over compensated by the absorption loss in the layer itself. For this reason, it is favourable to limit the refractive index to values around 2.0. We have fabricated mc-Silicon solar cells with our high quality silicon nitride as anti-reflection coating and also as a passivating layer, we obtained efficiency in excess of 14 % for the cells.

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