

Production Technology for Passivation of Polycrystalline Silicon Solar Cells

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Abstract

Techniques for cost-efficient operation of $\text{SiN}_x\text{:H}$ systems with a capability for hydrogen passivation in a manufacturing environment are analyzed. We conclude that $\text{SiN}_x\text{:H}$ performance may be optimized by a variety of techniques, and that the cost and productivity of the deposition tool may be the determining factors in the industry's decision for a particular technique. PECVD constitutes the current benchmark. Dual magnetron reactive sputtering is a candidate to achieve industry acceptance.

Introduction

Shipments of solar electric power products based on crystalline-silicon materials reached 321.6 megawatts (MW) in 2001 [1], representing more than 82% of total solar cell shipments. More than 57% of the crystalline silicon capacity, as well as most of the 40% expansion in shipments from 2000 to 2001 and the announced future additions, are based on multicrystalline silicon wafers.

Multicrystalline silicon and other low-cost substrates used for commercial Si solar cells contain high concentrations of impurities and defects [2]. Fabrication of high-efficiency devices requires their concentrations be greatly reduced and/or their electrical activity be diminished. Because some of the processes, such as phosphorous diffusion and Al alloying (for formation of the n+/p junction and metal contact, respectively) can remove many impurities and defects by gettering, the completed cell carries significantly lower impurity and defect concentrations than the starting material. Consequently, these processes are designed to optimize impurity gettering in commercial solar cell fabrication. However, even after optimized gettering, significant amounts of impurities remain in the cell. Use of hydrogen passivation is one way to mitigate the effects of the residual impurities and defects [3].

A number of methods have been applied for hydrogenation of Si solar cells including ion implantation, plasma processing, forming gas anneal, and, more recently, PECVD nitridation. Crystalline-silicon cell manufacturing is converging on a set of standard production tools [4]. Typically used are CVD of antireflection TiO_2 or $\text{SiN}_x\text{:H}$ layers and printing and firing of a thick film paste (TFP) metallization. PECVD nitridation involves deposition of an antireflection $\text{SiN}_x\text{:H}$ layer, followed by screen printing and firing of the metallization through the nitride using a rapid thermal anneal (RTP). For multicrystalline silicon wafers, efficiency gains from the use of PECVD $\text{SiN}_x\text{:H}$ layers, as opposed to TiO_2 , are reported to be well over 10%. In an era of new

factories with capacities in the hundreds of MW, there are major opportunities for PECVD and other cost-effective $\text{SiN}_x\text{:H}$ deposition tools.

This paper presents the key conclusions of a model that explains hydrogen diffusion during a $\text{SiN}_x\text{:H}$ deposition process followed by RTP. We then review the major techniques for $\text{SiN}_x\text{:H}$ deposition with intrinsic ability for impurity and defect passivation. We finally evaluate the performance potential of processes suitable for passivation in an industrial setting. As a result we determine that, in addition to PECVD, use of a dual magnetron reactive sputtering process has considerable potential in mass manufacturing of silicon solar cells.

Mechanisms of H Diffusion in a Nitridation Process

It is now known that a nitridation process involving PECVD $\text{SiN}_x\text{:H}$ films produces bulk passivation of multicrystalline Si solar cells. It is generally contemplated that the passivation mechanism is the diffusion of hydrogen from SiN_x film into the Si, during deposition or during post-deposition anneal. Some authors have suggested that in a nitride process, hydrogenation occurs during RTP step when H released from $\text{SiN}_x\text{:H}$ diffuses into Si [3,4]. This explanation does not consider H diffusion into Si during the nitridation itself. Recently, we have developed a model for diffusion of H in Si containing impurities and defects [5,6]. It shows, through quantitative modeling, that H can be introduced into traps near the surface of Si solar cells during nitridation. This “stored” H is de-trapped and redistributed during subsequent RTP anneal. This mechanism explains most observations related to solar cell passivation.

We have performed calculations for many cases, from which we can summarize some salient conclusions.

- In a two-step $\text{SiN}_x\text{:H}$ passivation process, the deposition step is accompanied by a shallow diffusion of H, in which H is “stored” near the wafer surface. The process-induced-trap (PIT) density controls the profile of the H, whereas the bulk trap density determines the depth of such diffusion.
- In the anneal step, the source of H can be simply the in-diffused H. It may be pointed out that although H will be depleted out of $\text{SiN}_x\text{:H}$ film during this step, there is no indication that any H from this film is going into the wafer. A simple redistribution of H is sufficient for effective passivation.
- The diffusion depth of H upon annealing is strongly controlled by the bulk trap density. For example, if the bulk trap density is $1\text{E}16\text{ cm}^{-3}$, the H will permeate through the entire wafer in a 1s anneal at 800°C . This is in agreement with experimental observations [3].
- Because the trap density and distribution play a dominant role in the diffusion of H, it is clear that lower trap density material will require shorter anneal time or lower temperature. Likewise, higher predeposition temperatures during deposition can help introduce higher H content necessary to passivate higher trap and impurity concentrations. An interesting effect of the RTP step is that it can anneal out the plasma process-induced defects, making the H available for passivation.

To verify this theory, we measured the H profiles in the solar cell after PECVD nitridation and after subsequent RTP step in ASE America’s production solar cells. For these measurements, the $\text{SiN}_x\text{:H}$ films were removed from solar cells with AR coating (no RTP) and after metallization firing (without affecting the H in the cell). Figure 1 shows the measured profiles that clearly demonstrate the presence of H in the solar cell after nitridation, and a redistribution of the

existing H. The H profiles match very closely those predicted by our theory. These results clearly suggest that any $\text{SiN}_x\text{:H}$ deposition process, that creates a surface damage and simultaneously exposes the surface to atomic H-containing ambient can produce a reservoir of H at the surface. Subsequent high-temperature process can release this stored H to passivate bulk defects and impurities.

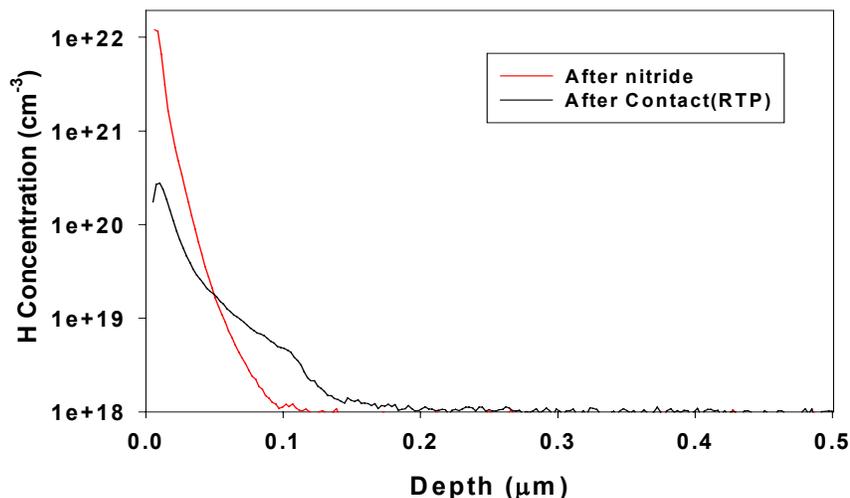


Figure 1: SIMS profiles of H in EFG ribbon samples: **Red:** after PECVD Si_3N_4 coating, **Black:** after contact firing (RTP).

Plasma Enhanced CVD $\text{SiN}_x\text{:H}$ Deposition and Properties

Amorphous silicon nitride (SiN_x) thin films have many applications in the semiconductor industry and in photovoltaics. SiN_x is an effective diffusion barrier against moisture and alkali impurities, which, when coupled with a high dielectric constant of 7.5, becomes an ideal candidate material for gate dielectric [7]. For solar cell and other advanced device applications in which low processing temperatures are required, SiN_x films are deposited by PECVD from a mixture of SiH_4 and NH_3 at process temperatures $\leq 400^\circ\text{C}$, which are compatible with commercial manufacturing processes [8]. The resulting films are hydrogenated amorphous SiN_x and are an excellent barrier against hydrogen out-diffusion.

Optical and electrical properties of the films depend on the structure and the chemistry defined by the Si-H, N-H, Si-N bond densities, Si-to-N ratio, and the amount of unbound H, resulting in a wide range of properties. Typically, for films deposited from SiH_4 and NH_3 , local bonding depends on the N-to-Si ratio “x” in the films [9]. For small x, the bonding configuration consists of isolated Si-H bonds, with no adjacent Si-N bond. As x increases, multi-N-bonded Si-H bonds dominate the structure. Finally, for $x > 1$, N-H bonds start to form and increase with x. Material properties of the SiN_x films, such as refractive index, ESR spin density, band gap and Urbach tail, can be adjusted across a wide range by changing N content. SiH_4 and N_2 can be used to deposit silicon nitride by PECVD, but these reactants typically yield silicon-rich films because of the relatively high bond energy of N_2 . SiH_4 and NH_3 depositions are normally carried out at pressures of 0.2 to 3 Torr, which yield growth rates of 20 to 50 nm/min. PECVD silicon-nitride films contain 15% to 30% of hydrogen bonded to either silicon or nitrogen [10].

The refractive index of SiN_x depends on processing parameters and stoichiometry. It is greater than 2.0 at 630 nm, which makes it an ideal single-layer AR coating for amorphous and crystalline solar cells [11]. PECVD SiN_x films are effective for surface passivation of silicon solar cells. Surface passivation effectiveness depends on the deposition method. Ion bombardment during deposition creates different defect types at the Si- SiN_x interface. Substrate temperature is a most important deposition parameter determining hydrogen content and is anti-correlated to the surface recombination velocity [12,13].

Bulk passivation of multicrystalline Si solar cells by PECVD $\text{SiN}_x\text{:H}$ films has been analyzed by Fukui, et al. [14]. The passivation mechanism is the diffusion of hydrogen from SiN_x film into the Si, during deposition or during post-deposition anneal, and the saturation of the dangling bonds associated with various defects in the material by this hydrogen. Fukui measured a decrease in the ESR spin density from $4 \times 10^{14} \text{ cm}^{-3}$ to $2 \times 10^{14} \text{ cm}^{-3}$ as a result of SiN_x coating of the solar cell from three different sources.

For microelectronic applications such as gate dielectrics, SiN_x films are required to have high resistivities and breakdown voltages. In a- $\text{SiN}_x\text{:H}$ films these electrical properties are inversely correlated to the hydrogen content of the films [15]. PECVD films with low hydrogen content can be obtained only at high substrate temperatures of $\geq 300^\circ\text{C}$. Electron cyclotron resonance PECVD (ECR-PECVD) [16] can yield low-hydrogen-content films at low temperatures and was originally developed for this application. In ECR-PECVD, a highly ionized plasma ($\sim 10^{16} \text{ m}^{-3}$) can be produced as a result of high electron temperatures because of the combined effect of the microwave radiation (2.45 GHz) and the magnetic field. In such nitrogen plasma, there is a high degree of dissociation of N_2 molecules, which allows gas phase reactions with SiH_4 molecules and results in a material with lower hydrogen content than is obtained with NH_3 . Recently, Soppe et al. investigated the application of ECR-PECVD deposited SiN_x films to surface passivation of silicon cells [17], showing that SiN_x films deposited from SiH_4 and NH_3 precursors onto FZ-Si result in a surface recombination velocity as low as 50 cm/s for a deposition temperature of 475°C . Recombination increases to 500 cm/s for a deposition temperature of 300°C , which is due presumably to the increase in the hydrogen content of the film from 12.8 at% at 475°C to ≈ 5 at%. This is consistent with what is observed in the case of PECVD SiN_x . The authors also demonstrated bulk passivation of microcrystalline Si solar cells by comparing device characteristics of annealed SiN_x -coated solar cells to the as-coated solar cells. Annealed solar cells showed a 1% average absolute higher efficiency than the as-deposited ones, indicating bulk passivation caused by hydrogen in-diffusion from the SiN_x .

Industrial Plasma Enhanced CVD $\text{SiN}_x\text{:H}$ Systems

An ECR-PECVD in-line system manufactured by Roth & Rau is the current industry benchmark. The Roth & Rau SiNA is a high-throughput, five-chamber continuous in-line system in which cells are transported on carriers. More detail about the system and its performance is given in reference [18]. Deposition is of the remote plasma type in which the linear level source operates at 2.45 GHz frequency. Water-cooled permanent magnets confine the NH_3 plasma and increase the ionization rate. SiH_4 is introduced at the substrate. For a film thickness of 80 nm, a cell tray can be loaded every 90 s into a system utilizing four linear sources in series. Standard operating temperature is 350°C , but it can be as high as 450°C .

Shimadzu (Japan) supplies a direct PECVD System. Shimadzu literature describes the reactor as a quasi-continuous, in-line system with four vacuum chambers isolated by gate valves. Substrate

trays preheated in an external oven are further heated in the load-lock chamber from the top and bottom via lamp heaters. From the load-lock chamber, the trays move into two process chambers in which SiN_x films are deposited on stationary trays heated by resistive heaters. Standard deposition temperature is 450°C , but can be as high as 550°C . Deposition is obtained by supplying microwave (90–460 kHz) power to an electrode facing the tray in the presence of a SiH_4 , NH_3 , and N_2 mixture. From the process chamber, the tray moves into the unloading chamber and is removed from the system. Effective deposition rate is quoted to be $200 \text{ \AA}/\text{min}$, which gives, for an 800-\AA film, an effective process time of 4 min. Other commercial reactors based on multi-tube batch systems have lower productivity.

Sputtered $\text{SiN}_x\text{:H}$ Deposition and Properties

Commercial viability for large-area, high-throughput manufacturing attracts interest in the sputtering process. Manufacturing of Si PV modules, thin-film transistor (TFT) arrays for large-area liquid crystal displays (LCDs), 2D imagers, scanners, and detectors all require low-cost deposition of SiN_x films. The advantages of sputtering versus PECVD include low-temperature processing, use of nontoxic gas, high deposition rate, low downtime due to direct deposition, and high homogeneity/uniformity on very large surfaces. Several researchers have studied, in detail, the reactive sputtering for silicon nitride films [19,20] for microelectronic applications such as oxidation masks, gate dielectrics, inter level insulators, and final passivation layers (see for example [21]), showing that the silicon-nitride film properties can be greatly varied with the preparation conditions.

Although reactive magnetron sputtering can be used to deposit silicon-nitride films for Si solar cells and in microelectronics, it has a number of limitations (such as arcing, disappearing anode and low deposition rate) that prevent its acceptance for large-scale manufacturing [22]. These problems can be addressed by the use of dual magnetron sputtering (DMS), in which an AC power having a frequency larger than 10 kHz is connected to the two targets so that they are driven alternatively positive and negative with respect to one another [23]. This arrangement permits each target to act as an anode for the other. If the reversal frequency is high enough, only a very thin layer of insulator will be formed on the target acting as an anode, and this very thin layer can be sputtered away. Note that when the target acts as an anode it collects electrons; these not only provide the return current for the sputtering process, but also discharge any supply accumulated positive charges on insulating islands on the target, thus reducing cathode arcing. TwinMag is such a DMS system that uses 40 kHz AC power [24]. The TwinMag sputtering system has high potential for fast and stable reactive deposition of $\text{SiN}_x\text{:H}$. The system used by Preu et al. to study AR and passivation effect of SiN_x films on Si solar cells is said to be capable of operating continuously for 310 hours at a dynamic deposition rate of $35 \text{ nm m}/\text{min}$ [25]. This means that the layer thickness will be 35 nm if the substrate passes one TwinMag with a speed of $1 \text{ m}/\text{min}$. Linear sources up to 3.75 m have been developed to coat 3.2-m-wide substrates with a thickness uniformity of $\pm 1.5\%$. The study demonstrated that SiN_x films reduced S_{eff} to $< 1000 \text{ cm}/\text{s}$ from $10^6 \text{ cm}/\text{s}$. Also, based on the measured open-circuit voltages, the deposition process did not introduce any damage to the emitter and/or the space charge region. The gain in the short-circuit current resulting from the AR effect was as high as 39%. It should be pointed out that even though the authors prepared hydrogenated SiN_x films by introducing H_2 into the sputtering gas, they did not determine the bulk passivation effect of such films on multicrystalline Si solar cells. Information on industrial sputtering systems such as a dual-magnetron sputtering system developed by Balzers Process Systems (BPS) [25] is limited.

Performance and Cost of SiN_x:H Deposition Tools

In the preceding sections, we have seen that PECVD and sputtered SiN_x layers can be fabricated with a large range of properties suitable for solar cell application. However, although hydrogenated SiN_x films were prepared by introducing H₂ into the reactive sputtering gas, no data are available on the effect of such films on bulk passivation multicrystalline Si solar cells.

Although the question of the applicability of sputtering to nitridation awaits experimental verification, our model for hydrogen diffusion during a SiN_x:H plus RTP deposition process predicts that sputter deposition is amenable to optimization for bulk passivation. We expect that the optimum near-surface conditions for shallow diffusion of H in the deposition step, and H “storage” near the wafer surface, can be obtained by careful tailoring of the PIT profile by controlled damage of a near-surface layer during sputtering.

The second key question about sputtering regards tool cost. In analyzing production tools, it is useful to employ the concept of cost of ownership (CoO), defined as “the full cost of embedding, operating, and decommissioning in a factory environment a process system needed to accommodate the required volume of product material” (SEMI Standard E-35: Cost of Ownership for Semiconductor Manufacturing Equipment). The algorithm for CoO (Equation 1) includes the fixed costs FC, the running costs RC, the yield cost YC, the equipment life L, throughput T, yield Y, and utilization U:

$$\text{CoO} = [\text{FC} + \text{RC} + \text{YC}] / (\text{L} \cdot \text{T} \cdot \text{Y} \cdot \text{U}) \quad \text{Equation 1}$$

The CoO of PECVD silicon nitride deposited by the Roth & Rau machine has been calculated to be 0.04 €/Wp [18]. This value is lower than earlier estimates of [26], reflecting the progress in industrial PECVD technology.

The estimated CoO for sputtered silicon-nitride films has been estimated to be 0.043 €/Wp, comparable to the cost of PECVD films. However, a calculation from [25] of the area throughput of a sputtering system with two TwinMag sources in series suggests that a useful area of about 3.2 m² per min can be coated with SiN_x:H. Assuming 15%-efficient cells, we estimate a capacity of about 50 MW per year per 2,000-hour shift for such a machine. Such a high throughput can reduce the fixed costs (FC), which are a significant component of CoO. Conveniently, the process uses no SiH₄ or NH₃ gases. If the cost of silicon targets can be controlled, we expect that the ‘learning curve’ of industrial SiN_x:H sputtering will lead to CoO decreases for sputtering technology similar to those achieved in industrial PECVD nitride.

Conclusions and Recommendations

The review of the scientific literature and our current physical model presented earlier in this report suggest that the key solar cell bulk passivation properties of SiN_x films are, to a first order, independent of the processes used to deposit SiN_x films. In view of this fact, in choosing a particular process for the development of a commercial-scale SiN_x deposition system the primary criteria should be the suitability of that process to large-scale, high throughput manufacturing environment. PECVD SiN_x:H is the current technology of choice. Dual magnetron reactive sputtering from intrinsic silicon targets is a potential competitor. Continuous in-line sputtering is a well-developed technique to deposit thin films over large areas at high throughput. Sputtering from silicon targets in the presence of N₂ and H₂ avoids the use of dangerous gases such as SiH₄ and NH₃ which require care in handling, as well as complicated systems to safely dispose of them, especially when the utilization rates are as low as in the plasma-assisted deposition

systems. Dual magnetron reactive sputtering of insulators from elemental targets is the preferred sputter deposition technique of insulators because of its high deposition rate and stable operation over extended times.

The further development of both technologies requires increased knowledge of (1) the kinetics of H diffusion from the SiN_x film, and (2) the amount of hydrogen required to bulk passivate a typical multicrystalline silicon wafer, and (3) verification of bulk passivation by sputtered silicon nitride. Optimum operating parameters of a dual magnetron system need to be determined on a laboratory-scale, in-line system.

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