



## Review

## Chemically active plasmas for surface passivation of Si photovoltaics

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## ABSTRACT

The plasma catalyzed deposition of compound dielectrics is very common for surface passivation of Si-based solar cells in recent decades. This paper reviews the underlying physics and chemistry of chemically active plasmas for the deposition of dielectric films including hydrogenated amorphous silicon nitride (a-SiN<sub>x</sub>:H), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and hydrogenated amorphous silicon oxide (a-SiO<sub>x</sub>:H). The relevant growth and passivation mechanisms are identified and several examples are selected to represent the superiority of plasma processes in the application of Si photovoltaics.

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## 1. Introduction

A number of low-temperature, chemically active plasma sources and plasma facilities such as capacitively coupled radio-frequency (RF) plasma-enhanced chemical vapor deposition (PECVD) [1–5], very high frequency (VHF) PECVD [6–11], microwave plasma (MP) CVD [12–16] and inductively coupled plasma (ICP) CVD [17–19] have found numerous applications in the fabrication of silicon

photovoltaic (PV) devices including bulk Si wafer solar cells and Si thin-film solar cells. These plasma processes have two general targets: increasing energy conversion efficiency and reducing the production cost of PV devices. In order to improve the conversion efficiency, the plasma tools are used to create well-organized small features, such as nanoscale structures and textures for light trapping effect, as well as to deposit high-quality dielectric thin films with excellent passivation and antireflection performances. For reducing the production cost, many low-cost plasma activated synthesis processes have been tested in place of traditional existing processes or added to the standard process sequence of Si-based solar cells. Due to the growing consensus that both energy crisis and climate change are inevitable and that the solar energy may have to serve as the main energy source in the future, low-temperature reactive plasmas are believed to play a key role in

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developing a cleaner and more environmentally conscious world, especially in developing PV power as a clean, inexpensive and sustainable energy source [20].

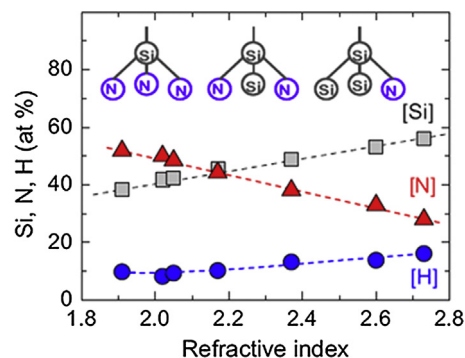
Both the plasma catalyzed deposition of Si-based thin films and the plasma species interaction with Si materials via plasma surface chemistry and engineering are one of the forefront research areas which encompasses elements of physics of plasmas, radical creation, materials science and engineering, structural chemistry and some other areas. The readers who are interested in these areas can be referred to our previous review article [21], which systematically and comprehensively discusses the effects of low-temperature plasma dissociation and deposition on the synthesis of Si-based thin films as well as the low-temperature plasma interactions with Si materials. Apart from these plasma applications highly related to Si materials, some compound dielectric thin films, such as hydrogenated amorphous silicon nitride (a-SiN<sub>x</sub>:H), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and hydrogenated amorphous silicon oxide (a-SiO<sub>x</sub>:H) synthesized via chemically active plasma processing, enable new exotic functionalities such as surface passivation and surface antireflection for Si PVs. According to the working principle of a Si solar cell, where electron–hole pairs are generated by the incident illumination and then separated to flow out, high-efficiency Si solar cells can be obtained only when both the loss of photo-generated carriers and the loss of sunlight entering into solar cells are reduced [22]. In other words, the effective minority carrier lifetime ( $\tau_{\text{eff}}$ ) should be lengthened and the surface-reflection loss of sunlight should be reduced. To enhance the  $\tau_{\text{eff}}$ , the surface recombination of photo-generated carriers has to be minimized by using a passivation layer (a reduction in surface recombination is usually called surface passivation). To reduce the optical loss due to the reflection at the air/c-Si interface, the use of an anti-reflective layer is preferred.

In this paper, we examine the main characteristics of low-temperature, chemically active plasmas for the deposition of compound dielectrics including a-SiN<sub>x</sub>:H, Al<sub>2</sub>O<sub>3</sub> and a-SiO<sub>x</sub>:H that serve as the passivation layer for Si PVs. An overview on the physical and chemical elementary processes involved in the synthesis of these compound dielectric thin films is also presented. Their functionalities, namely passivation and antireflection performances, are pinpointed, and the relationship between the plasma processes and the resultant performances are also identified. Here we will not elaborate on amorphous silicon (a-Si:H) though it is an extremely good passivation layer. In fact, a-Si:H is a semiconductor material which serves as not only the passivation scheme but also the base and emitter for Si solar cells. The relevant growth mechanism and passivation properties can be referred to our previous publications [21,23].

## 2. Silicon nitride

Amorphous hydrogenated silicon nitride (a-SiN<sub>x</sub>:H or SiN<sub>x</sub> for brevity) films deposited by PECVD or MW-PECVD have become the industry standard for application of anti-reflection coating layer (ARC) and passivation layer on screen-printed crystalline silicon wafer solar cells including monocrystalline silicon (c-Si) and polycrystalline silicon (poly-Si) [24–29]. Extensive research has been led during the last several decades, producing SiN<sub>x</sub> films that offer excellent surface passivation, transparency and antireflective properties, stability under ultraviolet light exposure and under high thermal treatments [30,31]. The expansion of this low temperature, reactive plasma technology is due to a substantial improvement in solar cell efficiency resulting from the deposition of SiN<sub>x</sub> in conjunction with fire-through techniques for the metallization step.

This enhancement can be attributed to three driving forces. First, a large amount of hydrogen originating from the plasma



**Fig. 1.** Composition of a-SiN<sub>x</sub>:H films in terms of H, Si, and N density as a function of the refractive index. The films were deposited in a Roth & Rau MW-PECVD reactor. The atomic densities were obtained by Rutherford backscattering spectroscopy and elastic recoil detection. The inset shows some possible bonding configurations of Si (with dangling bonds) where N<sub>3</sub>=Si- represents the amphoteric K-center, which is typically positively charged for a-SiN<sub>x</sub>:H films on Si substrates. Reprinted from Dingemans et al.<sup>35</sup> Copyright 2012: American Institute of Physics.

gas dissociation and incorporated in the SiN<sub>x</sub> film can be driven into the solar cell during the metallization step, leading to a good bulk passivation for c-Si or poly-Si solar cells [32,33]. This effect is particularly significant for poly-Si solar cells [29,33,34] since poly-Si contains various types of defects in the bulk.

The second driving force is the antireflective properties of the nitride layer which reduce the light reflection significantly. The relatively high and tunable refractive index (~1.9–2.3) of a-SiN<sub>x</sub>:H makes the material suitable as an antireflective coating on silicon. A representative plot (see Fig. 1) presents the material composition in terms of the atomic H, Si, and N density as a function of the refractive index [35]. The films were deposited in a Roth & Rau MW-PECVD reactor and the atomic densities were obtained by Rutherford backscattering spectroscopy and elastic recoil detection. Films with comparatively high nitrogen content (N-rich SiN<sub>x</sub>) exhibit refractive indices of approximately 2, which results in optimal antireflection properties when applied on the front side of a solar cell. In contrast, films with low nitrogen content (Si-rich SiN<sub>x</sub>) show higher refractive indexes and therefore higher extinction coefficients, leading to some absorption of light within the film that degrades the antireflection effect. The films also contain a relatively large amount of hydrogen of ~10–30%, which plays as the first driving force.

The third driving force is the surface passivation effect, which is achieved by chemical passivation or/and field-effect passivation. The chemical passivation aims to reduce the surface defects by saturating the remaining silicon dangling bonds. Technologically, this strategy is much more sensitive to the presence of defects at the surface than the field-effect passivation and usually related to a passivating layer deposited or grown over the silicon surface. The field effect passivation consists of producing a band bending at the silicon surface, thus creating an electric field. This electric field will make one type of carriers hard to reach the surface defect center. Therefore, the recombination rate is strongly reduced since two types of carriers, namely electrons and holes, are needed to complete the recombination process at the surface defect center.

For the PV applications, plasma deposition of a-SiN<sub>x</sub>:H can be obtained with various precursor gases but most commonly used are combination of either SiH<sub>4</sub> and NH<sub>3</sub> or SiH<sub>4</sub> and N<sub>2</sub>. For both cases, silane simultaneously acts as silicon and hydrogen source. For the case of SiH<sub>4</sub> and NH<sub>3</sub>, however, the ammonia in addition to being a source of nitrogen has a tendency to deposit a-SiN<sub>x</sub>:H with a high ratio of incorporated hydrogen [36]. In SiH<sub>4</sub> and NH<sub>3</sub> discharge, electron collisions with SiH<sub>4</sub> and NH<sub>3</sub> produce H, SiH<sub>3</sub>, SiH<sub>2</sub>, SiH

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