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Silicon carbon nitride films as passivation and antireflective coatings for silicon solar cells

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ABSTRACT

A new method to obtain antireflective and passivation layers for p-type silicon solar cells is presented. Hydrogenated silicon carbon nitride (SiC_xN_y:H) films are obtained by low frequency plasma enhanced chemical vapor deposition (PECVD), using ammonia (NH_3) and tetramethylsilane (TMS) as precursors; the influence of the deposition temperature and gas ratio on the film composition and properties is studied. It can be observed that the chemical composition of the film as well as its optical and passivation properties vary strongly with the gas ratio and temperature used. The optimal conditions with respect to the refractive index, the absorption coefficient and the minority carrier lifetime after rapid thermal annealing are determined. These conditions lead to an approximate stoichiometry of $SiC_{0.6}N_{0.8}$:H thin film including nearly 5×10^{21} cm^{-3} hydrogen bonds.

1. Introduction

The standard industrial process to obtain antireflective and passivating coatings is the deposition of hydrogenated silicon nitride (SiN_x:H) films by a low-frequency (LF) or a radio-frequency (RF) PECVD process, using silane (SiH_4) and ammonia (NH_3) mixtures [1]. One of the main drawbacks of these technologies is the use of the pyrophoric silane gas, which requires highly demanding storage and handling safety measures that lead to an increase in the overall cost of solar cell processing [2].

It has been shown that SiC_xN_y:H films with good passivation and optical properties can be obtained [2] and are therefore a practicable solution to replace SiN_x:H as antireflective and surface passivation layer for silicon solar cells [3]. The fact that the method here presented avoids the use of silane gas entails the potential to reduce the production costs of the solar cells. Furthermore it has been demonstrated that using SiC_xN_y:H films as passivation and antireflective coatings on boron doped p-type silicon solar cells can be beneficial, as it allows the diffusion of important quantities of carbon atoms into the silicon wafer, which combine with the existent oxygen atoms and permanently reduce the light induced degradation (LID) effect, due to the formation of boron–oxygen complexes [4]. Further, it has recently been shown that the replacement of the SiN_x:H by SiC_xN_y:H films can cause an augmentation of the solar cell shunt resistance and consequently increase the solar cell performance at low irradiation conditions [5].

This work proposes a silane-free process to obtain SiC_xN_y:H films to serve as antireflective and passivating coatings of p-type silicon solar cells. This method is based on the growth of SiC_xN_y:H films by low frequency PECVD, using tetramethylsilane (TMS) and ammonia (NH_3). TMS, Si $(CH_3)_4$, is a liquid organosilicon compound, with a vapor pressure at room temperature sufficiently high ($p_v \sim 600$ Torr) to sustain high gas flow rates without the need to heat the liquid line. TMS is a non-hazardous compound and its handling does not require any particular safety measures. The feasibility of this method was already demonstrated on previous publications [6–8]. In this article we present a detailed description of the chemical, optical and passivation properties of the films obtained. These properties are successively presented following the experimental description.

2. Experiment

The PECVD reactor and the process conditions will be first described, followed by the film characterization methods.

2.1. PECVD film deposition

The SiC_xN_y:H films were grown on a conventional Semco Engineering batch type low frequency PECVD reactor with a cylindrical quartz chamber horizontally positioned. In this reactor four parallel electrodes connected two by two sustain the plasma, which is created by a low frequency (35 kHz) plasma generator working in pulsed mode with $T_{on}/T_{off} = 10\%$ and a peak power of 1500 W. The standard deposition conditions used were: temperature, T = 400 °C, pressure, p = 1.8 Torr and the total gas flow ([TMS] + [NH_3]) of 500 sccm.

During this study the SiC_xN_y:H films were grown on commercial p-type monocrystalline silicon wafers obtained by Float Zone (FZ) and Czochralski (Cz) methods. The characterization of the passivation

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properties of the films was performed using 2" FZ p-type silicon wafers with a resistivity in the range 1–10 $\Omega \cdot$cm and a thickness of 275 μm. The thicknesses of the SiC_xN_y:H films obtained during this work were in the range 70–120 nm. To allow a straightforward characterization of the passivation behavior of the SiC_xN_y films, two identical coatings were grown on the two surfaces of the wafers.

During this work two different studies were made: one concerning the deposition temperature ranging from 300 °C to 450 °C and the other the gas concentration ratio, R = [TMS]/[NH$_3$] which varied from 0.015 to 0.5. During the temperature study, besides the experimental conditions described above, a gas ratio of R = 0.11 was established. To perform the gas ratio study a deposition temperature of 400 °C was used in all the tests.

In order to simulate the contact firing step that occurs during standard industrial solar cell processing, the SiC_xN_y:H films underwent a rapid thermal annealing (RTA) with a peak temperature of 810 °C in a JETFIRST RTA oven. All films were characterized before and after RTA.

2.2. Thin film characterization

2.2.1. Chemical characterization

The thin film chemical composition was determined by Electron Diffraction Spectrometry (EDS), X-ray Photoelectron Spectrometry (XPS) and Fourier Transform Infrared (FTIR) spectrometry.

The bond structure of the SiC_xN_y:H films was characterized by FTIR spectrometry using a Nicolet 6700 spectrometer in transmission mode, in the 650–4000 cm^{-1} range. It was assumed that the spectrometer response curve is the same over all the measuring range. To characterize each SiC_xN_y:H film, two absorption spectra were obtained, one from a silicon sample with the film grown and one from an equivalent silicon sample with no deposition (background); it is considered that the difference between these two spectra corresponds to the absorption spectrum of the SiC_xN_y:H film. The FTIR absorption spectra thus obtained were treated and the different peaks areas were determined using the spectroscopy software Grams/AI 9.1 [9]. The peak areas thus obtained are normalized to the film thickness. Using the normalized areas, the density of bounds, X–Y, was calculated according to the expression [10]:

$$X-Y = K \int \frac{\alpha(\omega)}{\omega} d\omega \qquad (1)$$

where K is the proportionality constant that corresponds to the inverse cross section of each absorption peak, α is the absorption coefficient and ω the wave number.

Since all the peaks were fitted to Gaussians the simplified expression was used:

$$X-Y = \frac{K}{\omega_{av}} \int \alpha(\omega) d\omega \qquad (2)$$

where ω_{av} is the wave number corresponding to the Gaussian center. The integral corresponds to the peak normalized area previously obtained, so by using the known values of K [10–12] presented in Table 1, the different bond densities can be obtained.

As previously mentioned the chemical composition of the SiC_xN_y:H films was further characterized by XPS and EDS measurements performed on thick (~800 nm) films obtained for this purpose. These techniques cannot detect light atoms like hydrogen but allow the determination of the atomic fractions of nitrogen, carbon and silicon in the films.

2.2.2. Ellipsometry measurements

The SiC_xN_y:H film thicknesses and optical properties were determined by spectroscopic ellipsometry measurements in the range 430 to 850 nm, using a Jobin-Yvon MM-16 spectroscopic ellipsometer.

Table 1
Infrared absorptions observed in the SiCxNy:H films.

Bond	Mode	Wave number (cm^{-1})	K (cm^{-2})	Ref.
Si – C	Si – C stretching	790	2.1×10^{19}	[10]
Si – N	N – Si$_3$ asymmetric stretching	850	2×10^{19}	[12]
Si – N	Si – N stretching of H – SiN$_3$	950	2×10^{19}	[12]
N – H	N – H wag–rocking	1150	2×10^{19}	[12]
Si – H	H – Si – Si$_3$	2000	7×10^{19}	[12]
Si – H	H – Si – HSi$_2$	2060	1.1×10^{20}	[12]
Si – H	H – Si – NSi$_2$	2100	1.7×10^{20}	[12]
Si – H	H – Si – SiN$_2$/H – Si – HSiN	2140	1.1×10^{20}	[12]
Si – H	H – Si – HN$_2$	2170	4.0×10^{20}	[12]
Si – H	H – Si – SiN$_3$	2220	2.0×10^{20}	[12]
C – H	C – H stretching	2890	2.5×10^{20}	[10]
N – H	N – H$\cdots$H stretching	3340	9×10^{19}	[12]
N – H	N – H stretching	3400	1.2×10^{20}	[11]

These measurements were then fitted using the New Amorphous model [13].

2.2.3. Carrier lifetime measurements

The characterization of the passivation properties of the SiC_xN_y:H films was performed by measuring the charge carrier effective lifetimes (τ_{eff}) with a Sinton WCT-120 Wafer Lifetime Tester using the Quasi-Steady-State Photoconductance (QSSPC) technique. For samples with higher lifetimes, these measures were complemented by measurements obtained in transient mode.

Since during the lifetime studies symmetrical SiCN/Si/SiCN structures were used, it can be considered that front and back surfaces have the same recombination behavior, i.e. $S_f = S_b = S$. By using the expression [14]

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S}{W} \qquad (3)$$

and assuming that for FZ wafers $1/\tau_{bulk} \approx 0$ the maximum surface recombination velocity can be estimated to be:

$$S_{eff} = \frac{W}{2\tau_{eff}} \qquad (4)$$

3. Results

The chemical composition of the SiC_xN_y:H films will be presented, followed by the description of the optical and passivation properties. The relation between the chemical composition and the optical and passivation properties of the SiC_xN_y:H films is discussed.

3.1. Chemical composition

3.1.1. EDS and XPS

The atomic compositions of SiC_xN_y:H films prepared with different gas ratios, obtained by both Electron Diffraction Spectrometry (EDS) and X-ray Photoelectron Spectrometry (XPS) measurements are presented in Fig. 1. The trend curves for the atomic fractions of the chemical species are also represented.

It is observed that, increasing the [TMS]/[NH$_3$] ratio, the atomic fraction of nitrogen is significantly decreased while the concentration of carbon increases strongly. The crossover between carbon and nitrogen atomic fractions takes place in the range 0.11 < R < 0.25. Such trends of N and C atoms were expectable since, for a constant total gas flow, increasing the gas ratio implies the increase of the carbon source (TMS) in the plasma and the reduction of the nitrogen source (NH$_3$). Less expectable was the observed reduction of the silicon content with the increase of the gas ratio; for R ≤ 0.25 the silicon fraction in the film is nearly constant, starting to diminish afterwards, as a steep