THE MAIN PROPERTIES OF AMORPHOUS ANTIREFLECTIVE COATING FOR SILICON SOLAR CELLS*

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Modification of solar cells by the use of antireflective coating (ARC) is very important for their final properties. Last time more frequently hydrogenated amorphous materials, for example silicon-nitrogen (a-Si:N:H) and silicon-carbon (a-Si:C:H), were applied as ARC on silicon solar cells. The authors developed the *Radio Frequency Plasma Enhanced Chemical Vapour Deposition Method* (RF PECVD) for preparation this films for potential optoelectronic applications. To obtain a-Si:N:H and a-Si:C:H films the gaseous mixtures SiH_4+CH_4 and SiH_4+NH_3 were used. On base of optical and structural research the main properties of amorphous films like: refractive index, reflection coefficient, thickness and hydrogen bondings content were found. Film structure was determined by the use *Fourier Transform Infrared Spectroscopy* (FTIR) and morphology was determined using a *Scanning Electron Microscopy* (SEM). The silicon substrates for solar cell constructions with discussed ARC revealed a considerable decrease in reflection coefficient. The results indicated that a-Si:N:H and a-Si:C:H are promising materials for improvement of solar cells efficiency.

Key words: antireflective coating, silicon solar cells
Słowa kluczowe: warstwa antyrefleksyjna, krzemowe ogniwo słoneczne

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1. INTRODUCTION

The use of amorphous films in optoelectronic devices is more frequent. Thin films for solar cells application can be categorized into two groups: one – as a device component, needed for the operation of the device and integrated as a part of the cell structure, second – as an aid in fabrication of solar cells from wafers [1]. Application of films as a device component in electronics and enables optical properties control. The optical properties of structures may be altered by thin films which act as antireflective coatings [2]. Additionally the important effect which is most influenced by amorphous hydrogenated silicon based films is surface passivation [3].

In this work, it is proposed to apply a-Si:C:H and a-Si:N:H thin films deposited by PECVD as antireflective coatings in multicrystalline silicon solar cells. Optical parameters and structural properties of these films are very encouraged.

2. EXPERIMENTAL

For obtaining amorphous hydrogenated thin films RF PECVD method at 13.56 MHz was used. Thin a-Si:C:H [4] and a-Si:N:H films [5] were deposited onto glass and mono- and multicrystalline silicon (Cz-Si and mc-Si). For this process two gas mixtures: SiH_4+CH_4 and SiH_4+NH_3 are employed. CH_4 and NH_3 content was in the range 14% to 75% and 11% to 30% for both mixtures, respectively. Other technological parameters were: RF power 5 W, substrate temperature of 180^{o}C, total pressure of 80 Pa and electrode distance of 15 mm. Changeable deposition time determines films thickness.

Main properties of a-Si:C:H and a-Si:N:H films were investigated by the use optical spectrometry (Perkin-Elmer Lambda 19 double beam spectrophotometer) [6], FTIR (Biorad FTS-60 V), SEM (NOVA NANO SEM 200, FEI Company) and Hommel Tester T500 profilometer [7]. Electrical parameters of silicon solar cells with and without antireflective coating were measured using computer controlled global spectrum sun simulator (I-V Curve Tracer For Solar Cells Qualification, v 4.1.1) [8] and were also simulated by the use PC1D computer programme [9].

3. RESULTS AND DISCUSSION

Determination of most important parameters of antireflective coatings was possible due to various measurements.

3.1. SEM measurements

SEM characterization was applied to mono- and multicrystalline silicon with and without ARC. The use of energy dispersive X-ray spectroscopy (EDS) makes possible a quantitative analysis of elemental composition of a-Si:C:H and a-Si:N:H. This method confirms that the increase in ammonia content in SiH_4+ NH_3 and methane content in SiH_4 + CH_4 causes the increase in nitrogen w_N = N/(N + Si) and carbon content w_C = C/(C + Si) in a-Si:N:H and a-Si:C:H films, respectively [7].

Multicrystalline silicon has very differentiated structure and for this reason composition analysis of films on mc-Si should be done in several points (Fig. 1). One can observed good homogeneity of film and good adhesion to basis. Unfortunately nitrogen content in areas between grains (point 1 and 2) and on tops of crystallites (point 3) is different (Tab. 1). Average values of N/(N+Si) taken from EDS measurements on area 0.0001 m^2 – it indicate that on whole surface similar nitrogen contents is observed.

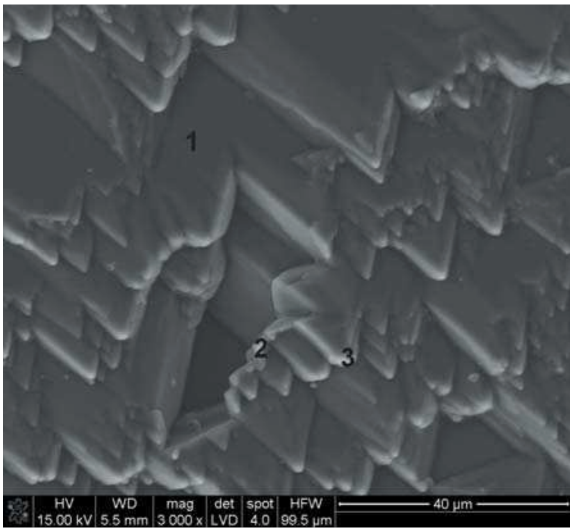

Fig. 1. SEM micrograph of mc-Si sample with a-Si:N:H obtained by PECVD in ammonia content w_a = $NH_3/(NH_3+SiH_4)$ = 0.22; elemental composition in points 1, 2 and 3 is describe in Tab. 1.

Rys. 1. Obraz SEM krzemu multikrystalicznego, pokrytego warstwą a-Si:N:H, otrzymaną metodą PECVD przy zawartości metanu w_a = $NH_3/(NH_3+SiH_4)$ = 0,22; skład chemiczny warstwy w punktach 1, 2 i 3 jest opisany w Tab. 1.

The content of carbon and nitrogen in films depends mainly on methane and ammonia concentration in gas mixture. Growth rate of films has also influence on film composition [5].

Table 1. Elemental composition of a-Si:N:H film of thickness of about 85 nm, obtained on mc-Si for w_a = 0.22. Average values of N/(N+Si) in two first rows were taken from EDS measurements on surface 0.0001 m^2.
Tabela 1. Skład chemiczny warstwy a-Si:N:H o grubości ~ 85 nm, otrzymanej na krzemie mc-Si dla zawartości amoniaku w mieszaninie gazowej w_a = 0,22. Średnia zawartość azotu N/(N+Si) w warstwie, w dwóch pierwszych wierszach, została oszacowana na podstawie pomiaru metodą EDS z powierzchni 0.0001 m^2.

	$NH_3/(NH_3+SiH_4)$	Atomic ratio of N/(N+Si)	Weight ratio of N/(N+Si)
SiN on Cz-Si	0,22	0,147	0,079
SiN on mc-Si		0,149	0,080
SiN on mc-Si, point 1		0,147	0,081
SiN on mc-Si, point 2		0,185	0,102
SiN on mc-Si, point 3		0,152	0,098

3.2. FTIR analysis

The concentration and kind of chemical bondings were studied by Fourier transform infrared spectroscopy in the absorption mode between 400 and 4000 cm^{-1}. The FTIR spectra of a-Si:C:H and a-Si:N:H films were presented in works [10] and [5]. Both types of films have many miscellaneous hydrogen bonds which are specified in Tab. 2. In a-Si:C:H films it is possible to distinguish numerous carbon-hydrogen and silicon-hydrogen bonds [10]. In a-Si:N:H we observed many nitrogen-hydrogen, silicon-hydrogen and hydrogen-silicon-nitrogen bonds [11]. All these hydrogen bonds are very advantageous for passivation process in multicrystalline silicon. Hydrogen diffuses deep into silicon structure and passivates residual impurities and defects like dangling bonds [1]. From the IR results for a-Si:C:H and a-Si:N:H films can be conclude that with the increase in methane and ammonia partial pressure the SiH, Si-C, SiN and N-H intensity drastically decrease.

Table 2. Absorption bands observed for a-Si:C:H and a-Si:N:H antireflective coatings, obtained on Cz-Si.
Tabela 2. Mody absorpcyjne obserwowane dla warstw antyrefleksyjnych a-Si:C:H oraz a-Si:N:H, naniesionych na krzem monokrystaliczny Cz-Si.

Wavenumber and vibration modes for a-Si:C:H	Wavenumber and vibration modes for a-Si:N:H
670-680 cm^{-1} – Si-C stretching or *SiH* wagging	630-650 cm^{-1} – *SiH* wag-rocking
700-800 cm^{-1} – Si-C stretching or $Si\text{-}CH_3$ rocking or wagging	650-670 cm^{-1} – SiH_n wagging
1030 cm^{-1} – CH_2 (sp^3) bending	750-1050 cm^{-1} – SiN stretching
950–1100 cm^{-1} – CH_n wagging or rocking	850 cm^{-1} – $N\text{-}Si_3$ stretching symmetric
1240-1280 cm^{-1} – *CH* (sp^2) bending or *CH* (sp^3)	1020 cm^{-1} – SiN stretching of $H\text{-}SiN_3$
1325-1350 cm^{-1} – CH_3 (sp^3) bending	1150 cm^{-1} – *N-H* wag-rocking
1450 cm^{-1} – CH_2 (sp^2) bending or $Si\text{-}CH_2\text{-}Si$ scissoring	1150-1540 cm^{-1} – NH_n bending

3.3. Optical parameters of ARC

The refraction index (*n*) and optical absorption (α) were determined from optical measurements of transmission of a-Si:C:H and a-Si:N:H films from formula given by [12]. The use of Tauc method was applied for above mentioned alloys [13].

Generally the refractive index values of a-Si:C:H and a-Si:N:H films decreases with carbon and nitrogen content increase. Similarly the decrease in energy gap showing the exponential character was detected with carbon and nitrogen content increase (Fig. 2).

One of the most important parameter of antireflective coating is the reflection coefficient. Total reflectivity of silicon substrates (Cz-Si, mc-Si) with and without ARC was measured by the Perkin-Elmer spectrophotometer equipped with the integrating sphere in the wavelength range from 400 to 1100 nm. Spectral dependences of the total reflectivity of Cz-Si with a-Si:N:H and a-Si:C:H films are presented in Fig. 3.

The effective reflectivity coefficient R_{eff} is the special parameter which was calculated from equation given in [6]. It describes reflection as specific numerical value suitable to various sample comparison.

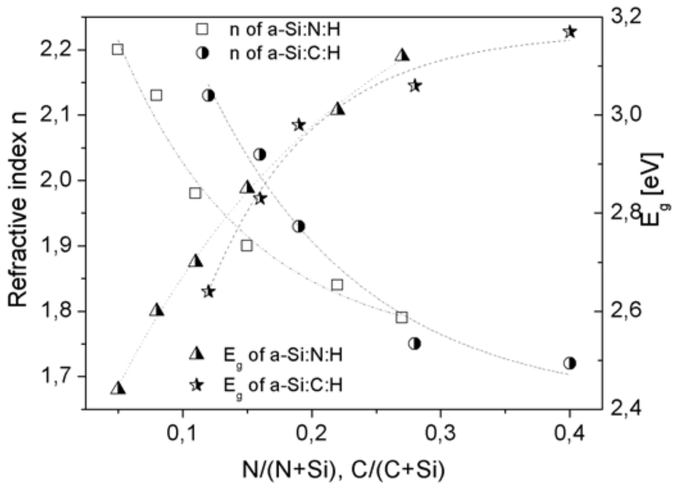

Fig. 2. The dependence of refractive index n and Tauc energy gap Eg on nitrogen and carbon content in a-Si:N:H and a-Si:C:H films, respectively.
Rys. 2. Zależność współczynnika załamania n oraz przerwy energetycznej Eg od zawartości azotu i węgla, odpowiednio w warstwach a-Si:N:H oraz a-Si:C:H.

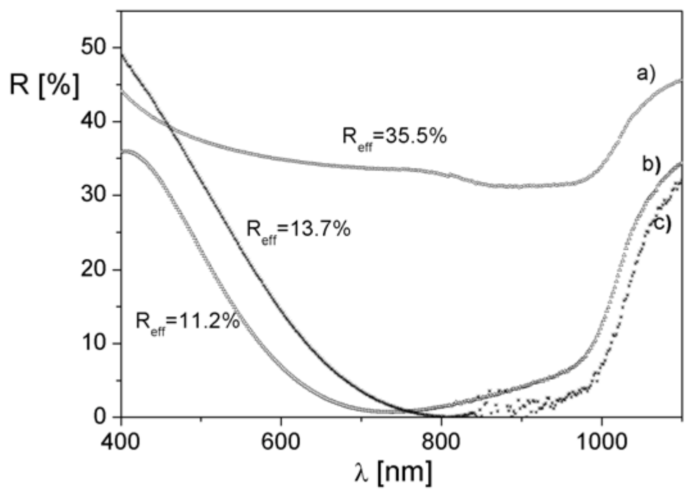

Fig. 3. Spectral dependence of the total reflectivity of: a) Cz-Si bare; b) Cz-Si covered by a-Si:C:H film of about 75 nm thickness; c) Cz-Si covered by a-Si:N:H film of about 85 nm thickness.
Rys. 3. Zależność odbicia całkowitego w funkcji długości fali: a) dla czystego podłoża Cz-Si; b) dla krzemu Cz-Si pokrytego warstwą a-Si:C:H; c) dla krzemu Cz-Si pokrytego warstwą a-Si:N:H

Effective reflectivity data for mc-si substrates (cells) with and without an ARC were analysed in [7]. For mc-Si bare it equal 26.6%, for mc-Si with a-Si:C:H film of about 70 nm thickness – 5.9% and for mc-Si with a-Si:N:H film of about 90 nm thickness – 8.2%.

Material parameters like refractive index and optical gap dependent on choosen technological regime affected final optimal properties of film for future optoelectronic application.

3.4. Parameters of multicrystalline silicon solar cells

Solar cells parameters were calulated by fitting of two diode model to the experimental data [14] and by the use PC1D computer programme [9].

Current-voltage I-V characteristic of multicrystalline silicon solar cells were measured under 1000 W/m^2 (AM1.5) irradiance. The cells were modified by the use of a-Si:C:H antireflective coating. Some results were presented in our previous paper [6]. The deposition of ARC coating apparently increases short circuit current I_{SC} and increasing solar cell efficiency from 8 to 11%.

Results from measurements of I-V characteristics of solar cells with and without antireflective coating were compared with results obtained from PC1D programme. These results explicitly indicate strong dependence of solar cells parameters from refractive index, thickness and reflectivity of ARC (Tab. 3).

Table 3. Photovoltaic output parameters for multicrystalline silicon solar cells (5 x 5 cm^2) with and without antireflective coatings ARC.

Tabela 3. Najważniejsze parametry eksploatacyjne ogniw słonecznych na bazie krzemu multikrystalicznego (5 x 5 cm^2), z i bez warstwy antyrefleksyjnej ARC.

Parameters of solar cell	without ARC	a-Si:C:H ARC	a-Si:N:H ARC
R_{eff} [%]	40	8	8
n	-	2.0	1.9
d [nm]	-	80	80
I_{SC} [A]	0.489	0.698	0.692
U_{OC} [V]	0.575	0.585	0.584
η [%]	8.11	11.78	11.66

Solar cells parameters are strongly influenced by the properties of deposited antireflective coating. It is evident that electrical parameters depend on optical properties of ARC. It is also known that the ARC plays a role of passivator of silicon defects.

4. CONCLUSIONS

PECVD is efficient method to obtaining good antireflective coatings. SEM spectra and EDS microanalysis confirm that a-Si:C:H and a-Si:N:H films characterized homogeneity and the uniform distribution of carbon, nitrogen and silicon. The surface of the obtained films is smooth. Both kinds of films have many different hydrogen bondings (FTIR analysis) which are very advantageous in passivation process of silicon defects. Additionally hydrogen present in the films may reduce the number of recombination centers. The optical parameters like refractive index and energy gap showed a correlation with technological process. The effective reflectivity of mono- and multicrystalline silicon is reduced after the deposition of a-Si:C:H and a-Si:N:H films. All properties of these films are very promising for applications as good antireflective coatings. Simulation method confirmed that solar cells with ARC with parameters characteristic to researched amorphous films exhibit the increase in efficiency and short circuit current. Real measurements of I-V characteristics of silicon solar cells are in good agreement with theoretical results and also show considerable increase in efficiency. Additionally these materials have proper optical properties for future applications.

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SUMMARY

NAJWAŻNIEJSZE WŁAŚCIWOŚCI AMORFICZNYCH WARSTW ANTYREFLEKSYJNYCH (ARC) DO ZASTOSOWAŃ W KRZEMOWYCH OGNIWACH SŁONECZNYCH

Modyfikowanie ogniw słonecznych z użyciem warstw antyrefleksyjnych (ARC – *antireflective coating*) jest bardzo ważnym procesem w aspekcie ich finalnych właściwości. W ostatnich latach coraz częściej stosuje się jako pokrycia antyrefleksyjne amorficzne warstwy uwodornione, np. warstwy a-Si:C:H lub a-Si:N:H. Do wytwarzania takich warstw autorzy wybrali metodę Chemicznego Osadzania z Fazy Gazowej, wspomaganego falami radiowymi (RFCVD - *Radio Frequency Plasma Enhanced Chemical Vapour Deposition*). W procesie otrzymywania warstw a-Si:C:H i a-Si:N:H zastosowano następujące mieszaniny gazowe: SiH_4+CH_4 oraz SiH_4+NH_3. Na podstawie optycznych i strukturalnych badań określono najważniejsze właściwości warstw antyrefleksyjnych: współczynnik załamania, współczynnik odbicia, grubość oraz rodzaj i koncentrację wiązań wodorowych. Struktura warstw była badana przy użyciu metody spektroskopii w podczerwieni (FTIR), a morfologia – mikroskopii skaningowej (SEM). Podłoża krzemowe do ogniw słonecznych, po-

kryte takimi warstwami, cechuje znaczna redukcja wartości współczynnika odbicia. Analiza charakterystyk prądowo-napięciowych ogniw słonecznych, zmodyfikowanych warstwami ARC, pokazuje znaczne zwiększenie ich sprawności i parametrów prądowych. Otrzymane rezultaty wskazują, że warstwy typu a-Si:C:H oraz a-Si:N:H są bardzo obiecującymi materiałami do tego typu zastosowań.