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OPTICAL AND MICROSTRUCTURAL PROPERTIES OF GRADED POROUS SILICON LAYER

OPTYCZNE I MIKROSTRUKTURALNE WŁASNOŚCI GRADIENTOWEJ WARSTWY Z POROWATEGO KRZEMU

In this work we present the results of investigations of porous silicon (PS) layers for solar cells application. The PS was formed by chemical etching (stain etching) of $n^+ - p$ Si substrate in a solution of HF, HNO₃ and H₂O. The dielectric response of a PS layer was modeled using a Bruggeman effective-medium approximation. It was shown that PS layer could be described by a model of graded layer with effective optical constants n_{eff} and k_{eff} changing from these of bulk material (silicon) to these of surrounding (air). The porosity of the PS layer changed from 10% near the bulk silicon region to nearly 85% at the silicon-air interface. The effective reflectance of Cz-Si surface decreased to about 5% after PS layer formation

Keywords: porous silicon, antireflection coating, graded layer

Przedstawiono wyniki badań własności optycznych i mikrostrukturalnych gradientowej warstwy z porowatego krzemu naniesionej metodą chemicznego trawienia. Podłożem były płytki polerowanego krzemu typu p z uformowanym złączem $n^+ - p$. Do symulacji własności wynikających z istniejącego gradientu założono wielowarstwową strukturę porowatego krzemu stosując przybliżenie Bruggeman'a efektywnego ośrodka. Określono wartości współczynnika załamania i ekstynkcji (n_{eff} i k_{eff}) w warstwie porowatego krzemu w funkcji długości fali światła oraz odległości od powierzchni krzemowego podłoża. Porowatość zmieniła się w granicach od 10% w pobliżu granicy podłoża-krzem porowaty do około 85% na granicy krzem porowaty-powietrze. Efektywny współczynnik odbicia dla krzemu z naniesioną warstwą porowatego krzemu wynosił tylko 5% w porównaniu z 25% wartością współczynnika odbicia od steksturyzowanej w KOH powierzchni multikrystalicznego krzemu.

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1. Introduction

Today, the crystalline silicon is the most important photovoltaic material. The production of modern, high-efficiency solar cells based on the multicrystalline p-type silicon (mc-Si) consists of the following steps: texturization, n^+ -p junction formation by phosphorous diffusion, deposition of a SiN_x antireflection coating (ARC) by Plasma Enhanced Chemical Vapour Deposition (PECVD), preparation of front and back metal contacts by the screen-printing method and co-firing of metalization in infrared furnaces. The texturization is commonly carried out by alkaline chemical etching, which is not effective due to different crystallographic grain orientation. The SiN_x is not only a good ARC, equally important is the fact that SiN_x reduces a surface recombination velocity and a bulk passivation is obtained during thermal treatment. However, the PECVD uses a very expensive and sophisticated deposition system. This is why some research groups try to simplify a technological procedure of ARC because the industrial applications require low cost ARCs. This is the case of porous silicon (PS), which exhibits very efficient ARC properties and provides partial surface passivation. Both electrochemical and chemical methods are used for the formation of PS ARC on n^+ -p silicon junctions [1-4]. Chemically etched (stain-etched) PS has a pronounced porosity gradient in depth, which is a result of a simultaneous etching at the PS/Si interface and Si dissolution throughout the existing porous layer. The effective refractive index n_{eff} of the PS depends on the porosity and morphology and can be closely matched to the optimal refractive index of an ARC for mc-Si solar cells. Wide-band ARCs could be formed by modulation of n_{eff} via the PS layer porosity [2]. Furthermore, a pronounced roughness at the PS/Si interface contributes to a uniform lowering of the reflectivity due to a texture-like behavior of the PS layer. The other advantages of forming the PS layer are: a reduction in a number of steps to produce a solar cell (PS could simultaneously replace three processing steps: texturization, passivation and ARC deposition) and low cost of the etching process.

The aim of this work was to study structural and optical properties of thin PS films formed by chemical (stain) etching of Si in HF-based solutions.

2. Experimental

Polished single crystal wafers of silicon (Cz-Si) p-type, $1 \Omega\text{cm}$ with n^+ -p junctions were used as a basic material. A n^+ -p junctions were formed by phosphorous diffusion from a POCl_3 source at 870°C . The sheet resistance of n^+ emitter layers was about $35 \Omega/\text{sq}$. The PS layers were formed on n^+ -p junctions by chemical etching in a modified $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}$ solution [4] during about 4 s. The microstructure of these samples was investigated with a Transmission Electron Microscope (TEM). The total reflectivity of silicon substrates with PS layers was measured using a Perkin-Elmer Lambda 19 spectrophotometer equipped with an integrating sphere.

3. Optical model of PS layer

In order to describe the optical properties of PS, which contains voids and interconnected small Si particles with different fractions in volume, the influence of the microstructure on the macroscopic dielectric response must be taken into account. When the wavelength of light is much larger than the typical nanocrystal size, the dielectric response of PS can be modeled using an effective-medium approximation [5, 6]. The total reflectivity spectra were simulated using a mixture of crystalline Si and voids in the Bruggeman effective-medium approximation. The Bruggeman model refers to the aggregate or random-mixture microstructure where two phases are inserted into the effective medium itself (which is the case in most thin layers). It is known that PSi obtained by chemical method is characterized by gradient porosity [3]. A multilayer structure was established in order to represent a porosity gradient in the PS layer perpendicular to the surface. The mixture ratio throughout the PS layer was assumed to be a linear interpolation of the mixture ratios at different specified depths ("nodes") within the layer. The node position was entered in percent of the total film thickness such that the first node position was at 0% (which was the closest to the substrate) and the last node at position 100%. Effective optical constants: the effective refractive index $n_{\text{eff}}(\lambda)$ and the effective extinction coefficient $k_{\text{eff}}(\lambda)$, the void fraction P at each node, the screening factor S and the total porous layer thickness d_{TOT} were the fit parameters. A Levenberg-Marquardt algorithm, which has become the standard of nonlinear least-square routines, was applied to optimize the multilayer structure and determine the fitted parameters [7]. When evaluating the model, our program solved a nonlinear equation to find all the roots of the Bruggeman equation and then picked only the physical solution to the dielectric function. To produce a good fit for the total reflectivity spectra of the PS layer, it was necessary to use the structure with eight nodes (seven sub-layers) (Fig. 3).

4. Results and discussion

TEM analysis of the chemically etched PS layers revealed a structural change in depth, which points out to the existence of strong porosity gradient throughout the porous structure. It means that the porosity is characterized by a graded transition from bulk to the surface i.e. the PS layer can be described by a model of gradient film with higher porosity at the surface and lower porosity at the PS/Si interface. A total porous layer thickness of about 160 nm can be derived from TEM micrograph (Fig.1).

Fig. 2 shows total reflectivity spectra of PS/n⁺-p Cz-Si structures for different etching times. The reflectivity spectrum of multicrystalline silicon (mc-Si) KOH texturized is also included for comparison. The effective reflectance R_{eff} [1] was calculated over the 400-1100 nm wavelength range under AM1.5 conditions. The pronounced reduction in the values of R_{eff} is caused by the PS layers formation.

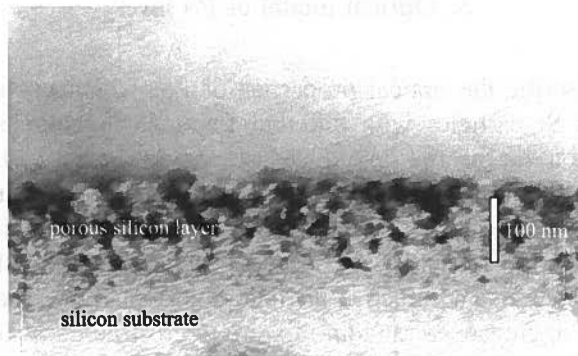


Fig. 1. TEM micrograph of a PS layer formed by the chemical method during 20 s etching

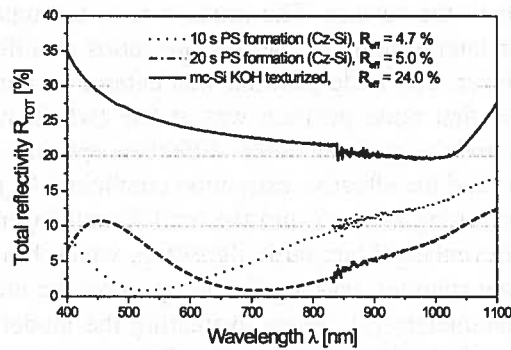


Fig. 2. Total reflectivity spectra of PS/ n^+ -p Cz-Si structures for different etching times. The reflectivity spectrum of a mc-Si KOH texturized is also shown. The effective reflectance R_{eff} was calculated over the 400-1100 nm wavelength range under AM1.5 conditions

To demonstrate the validity of our optical model the spectral reflectivity for a PS layer simulated on the basis of the fit results was compared to the measured total reflectivity as shown in Fig. 3. The positions of the minima and maxima observed in the calculated and measured spectrum are located at the same wavelengths. The observed deviations between the calculated and experimental spectrum are not critical, considering that they correspond to specular and total reflectivity, respectively. The fitted value of the total thickness of PS layer ($d_{TOT} = 163$ nm) is close to that determined from TEM. The other parameters obtained from the best fit of a PS layer: n_{eff} , k_{eff} and P as a function of wavelength λ and distance from the substrate surface d expressed in percent of the total layer thickness d_{TOT} are presented in Fig. 4 and 5. The effective optical constants of a PS layer are graded in the normal direction (perpendicular to the surface of the layer) from the values for bulk material (silicon substrate) to air medium. The P changes from 10% near the bulk silicon region to nearly 85% at the interface PS-air. It should be pointed out that the B r u g g e m a n

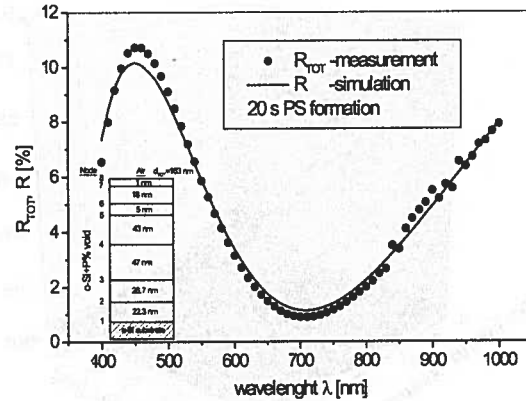
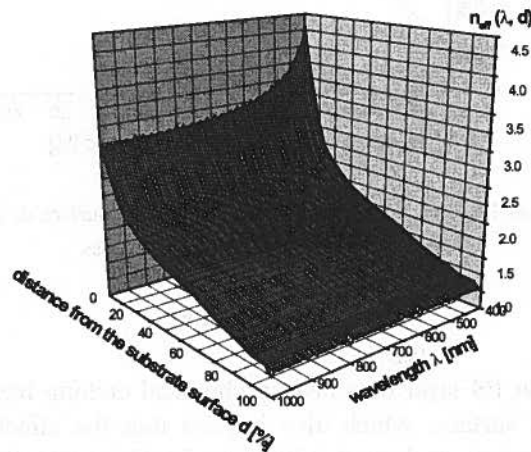


Fig. 3. Measured total reflectivity R_{TOT} of a PS layer (etching time 20 s) and spectral reflectivity R simulated for normal incident light on the basis the fit results

model works well up to 66% porosity because of the symmetry in treating both phases inserted into the effective medium. Above this value the Bruggeman model begins to describe a system in which the host material completely surrounds the second fraction like the Maxwell-Garnett model does. This means that the system gets more and more characteristic features of isolated particles with thinner and thinner connections the higher the porosity is. Despite those limits the Bruggeman effective medium approximation is often used to predict the structural and optical properties of PS layers [2, 3].



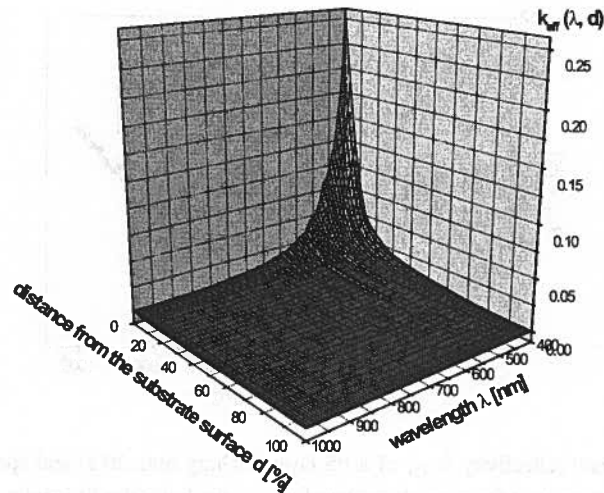


Fig. 4. Optical constants: n_{eff} (a) and k_{eff} (b) of a PS layer vs. wavelength γ and distance from the substrate surface d , which is determined in percent [%] of the total layer thickness

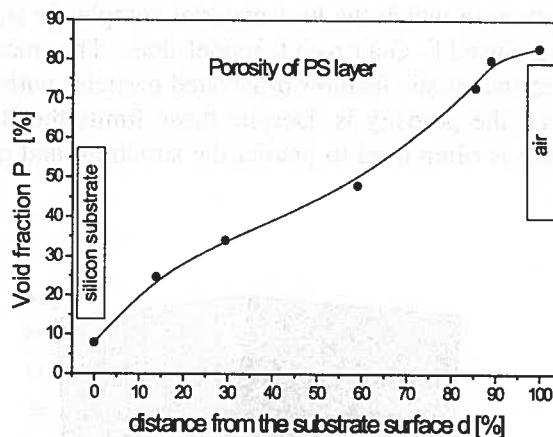


Fig. 5. Void fraction P of PS layer vs. distance from the substrate surface d , which is determined in percent [%] of the total layer thickness

5. Conclusions

It was shown that PS layer obtained by chemical etching has a porosity gradient perpendicular to the surface, which also implies that the effective refractive index changes in depth since it depends on the Si/void ratio. The total reflectivity spectra of PS layers were simulated using a mixture of crystalline Si and voids in the Bruggeman effective-medium approximation. A multilayer structure was established in order to

represent a porosity gradient in the PS layer. The good agreement between the measured reflectivity and the calculated reflectance of a structure having seven sub-layers was obtained.

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