
THE INFLUENCE OF SURFACE TEXTURE AND TEMPERATURE DEPOSITION OF TiO₂ LAYER ON CRYSTALLINE SILICON SOLAR CELLS PARAMETERS

Wpływ teksturowej powierzchniowej i temperatury osadzania warstwy TiO₂ na parametry krzemowych krystalicznych ogni słonecznych

In the present work, the investigation of the titanium dioxide (TiO₂) thin layer as an antireflection coating for silicon solar cells are presented. The TiO₂ layers were obtained by the chemical vapour deposition method using tetraethylorthotitanat (C₂H₅O)₂Ti at temperatures of the silicon wafers in the range from 150°C to 400°C. It has been established that all of the obtained TiO₂ layers contain anatase phase embedded in the amorphous background. A progress of the crystallization process with the increasing temperature of the substrate during the deposition has been observed. The change in opto-electronic parameters of silicon solar cells as a function of the deposition temperature of the antireflection coating has been discussed, taking into account the evolution of the crystallographic structure.

Keywords: titanium dioxide, antireflection coating, crystalline silicon solar cell

Praca przedstawia wyniki badań poświęconych zastosowaniu cienkich warstw TiO₂ jako powłok antyrefleksyjnych dla krzemowych ogni słonecznych. Warstwy TiO₂ wytwarzano metodą chemicznego osadzania z fazy gazowej (CVD) ze źródła ortotytaniantetraetyлу (C₂H₅O)₂Ti w zakresie temperatur płytek krzemowych od 150°C do 400°C. Stwierdzono, że wszystkie otrzymane warstwy TiO₂ charakteryzowały się amorficzna strukturą z wbudowaną fazą anatazu. Zaaobserwowano zwiększenie udziału fazy krystalicznej ze wzrostem temperatury krzemowego podłoża. Określono i przedyskutowano zmiany wartości parametrów opto-elektronicznych krzemowych ogni słonecznych w funkcji temperatury osadzania warstw antyrefleksyjnych TiO₂.

1. Introduction

Global production of solar cells continued its phenomenal growth, reached 2.520 GWp in 2006 year. The mono (Cz-Si) – and multicrystalline (mc-Si) silicon as a basis material continues to dominate the photovoltaic sector taking share 38% and 47%, respectively [1]. Advanced technology of the silicon solar cells requires surface structures enabling reduction of effective front reflection from 34.8%, for planar as-cut Si wafer below 10% in the range of 400–1100 nm electromagnetic radiation. On the other hand, the industrial application needs first of all high output with a low cost which eliminates many techniques and materials.

There are two main methods used in solar cells field and photovoltaic industry for the Si surface reflectance reduction – surface texturization (see Fig. 2) and antireflection coating deposition (ARC). The ARC plays a very important role in silicon solar cell production because of two main reasons: reduction of reflectivity and possibility to obtain good ohmic contact for front electrode simultaneously prevention of Si surface from contamination during co-firing process of front and back contacts. The widely applied in the industry are silicon nitride and titanium dioxide, this last one in low cost silicon solar cells, because the technology of deposition is very simple and easily, can be transferred to a production line without incurring high cost.

2. Experimental procedure

The silicon wafers were (100) Cz-Si, boron doped, p-type, 1 Ω·cm resistivity, 300 μm thick wafers denoted as samples Nos. 1 to 6 and mc-Si, boron doped, p-type,
1 Ω-cm resistivity, 300 μm thick as samples Nos. 7 to 12. This kind of Si wafers is used in mass scale industrial manufacturing of the silicon solar cells [2]. All samples were first etched in KOH(30%) to remove the saw damage of the material (10 μm thick from each side of wafers) and texturized in IPA:KOH(40%):DIH₂O in volume ratio 3:1:46 solution at 80°C for 15 min. and after that rinsed in HCl(2%) and HF(10%). All chemical processes were completed by rinsing in deionized water and drying in N₂. The emitter with the sheet resistance 40 Ω/□ was generated in an open quartz tube using liquid POCl₃ as the doping source, at temperature 840°C for 30 min. After diffusion the parasitic junction was removed by means a special Teflon clamp in which the wafers were immersed in HNO₃(65%):HF(40%):CH₃COOH(80%) solution in the volume ratio 5:3:3 for 1 min. Then phosphorus silicate glass was removed by immersion in a bath of HF(10%) for 2 min. The surface passivation was achieved by the growth of ~10 nm thick SiO₂ layer at the temperature of 800°C for 15 min in a controlled O₂ and N₂ atmosphere.

The Du Pont PV145 paste, for the front contact and the Ferro CN53-101 Al Conductor paste, for the back contact, were printed using 330 mesh screens. The silicon wafers, after drying at 150°C for 15 min, were co-fired in the infrared (IR) conveyor furnace, having three zones heated at temperatures 550°C, 650°C and 880°C, using the belt speed of 160 cm/min.

3. Structural and optical properties of TiO₂ and determination of a layer thickness

The crystallographic studies were performed on X’Pert MPD Phillips X-ray diffractometer in a grazing incidence configuration (GID). In this configuration the increase in the absorption path of the primary beam in a very thin layer is achieved by reducing the angle of incidence down to a few degrees. Figure 3 shows the diffraction patterns of TiO₂ films obtained at the different substrate temperature. All the layers contain anatase phase embedded in the amorphous background. As can be seen, the TiO₂ layers become more crystalline with an increase of the substrate temperature.

![Fig. 1. Scheme of the TiO₂ antireflection layer deposition system by CVD method](image)

![Fig. 2. SEM images of a surface texture obtained in KOH solution: (a) for Cz-Si, (b) for mc-Si](image)

In this work as antireflection layer for solar cells the titanium dioxide layer was deposited by the chemical vapour deposition (CVD) method with tetraethylorthotitanat (C₂H₅O₂)₄Ti, using purified nitrogen as a carrier gas (Fig. 1). The liquid source (C₂H₅O₂)₄Ti had vapoured at 200°C in a quartz bubbler and then it was transported to the Teflon nozzle (5 mm diameter) located 10 mm above the silicon wafer. The wafers were heated in the temperature range of 150°C – 400°C, at the step change of 50°C.

![Fig. 3. The influence of substrate temperature Tₛ on X-ray GID patterns of TiO₂ layers. Denotation A – anatase](image)

![Fig. 4. Grazing incidence X-ray reflectivity (GIXR) profile for TiO₂ deposited at 200°C. The best fit to the experimental data with the fitted parameter d = 33 nm is given by solid line](image)
The layer thicknesses were derived from grazing incidence X-ray reflectivity (GIXR) profiles for the TiO₂ layers. The GIXR is a technique based on the reflection of X-ray by a flat surfaces [3]. For a thin layer on the bulk substrate (Fig. 4) the reflectivity curve exhibits periodical oscillations called Kiessig fringes. They are similar to those observed in optics, due to the interference of X-rays at each defined interface. The layer thickness is determined from the angular distance between Kiessig fringes.

Transmission $T(\lambda)$ and reflection $R(\lambda)$ of the TiO₂ layers were measured with a Perkin Elmer U/VIS/NIR Lambda 19 spectrophotometer with an integrating sphere over the wavelength range $\lambda = 300$–$1300$ nm (Fig. 5).

$$n(\lambda) = A_n + \frac{10^B_n}{\lambda^2} + \frac{10^{12} C_n}{\lambda^4}$$ (1)

$$k(\lambda) = A_k + \frac{10^B_k}{\lambda^2} + \frac{10^{12} C_k}{\lambda^4}$$ (2)

where: $\lambda$ in [nm], $A_n$, $B_n$ and $C_n$ the material coefficients that define $n(\lambda)$, $A_k$, $B_k$ and $C_k$ the material coefficients that define $k(\lambda)$ (parameters of the fitting procedure).

The measured and fitted $T(\lambda)$, $R(\lambda)$ curves for one of the TiO₂ layer are shown in Fig. 6. The differences between the experimental and simulated spectra are within the measurement accuracy. The refractive index $n$ and the extinction coefficient $k$ vs. $\lambda$ show the dispersion typical for TiO₂ below the fundamental absorption edge [5]. It is particularly true for the layers obtained at the elevated substrate temperatures ($T_s = 300°C$, $400°C$). The overall increase in $n$ when the substrate temperature increases probably results from the increase in the layer density [6] (Fig. 7, 8).

The thicknesses shown in Fig. 5 have been extracted from GIXR profiles of the TiO₂ layers. The wavelength-dependent refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ were determined by fitting a single layer model to the data $T(\lambda)$ and $R(\lambda)$. The correlation for the $n$ and $k$ dispersive coefficients proposed by Cauchy have been applied. The Cauchy equations are empirical formulas which are best suited to model transparent materials (e.g. TiO₂) [4]. The equations 1 and 2 define the optical constants of the Cauchy material:

In the laboratory test for solar cell with TiO₂ ARC the best value of refractive index $n$ has the layer deposit-
ed at 400°C but for solar cells laminated in PV module, where there are capped with glass, the $n$ closed to 2 for the wavelengths longer than 450 nm is more optimal.

4. Measurements of solar cells electrical parameters

The I-V characteristics of solar cells were measured under standard test condition i.e. light spectrum AM1.5G, normalized to 1000 W/m² and 25°C cell temperature and the final data are collected in Tab. 1. A reference cell was calibrated at Wroclaw University of Technology in Photovoltaic Laboratory Solar Lab using B-class Sun simulator.

<table>
<thead>
<tr>
<th>Cell No.</th>
<th>Deposition temperature [°C]</th>
<th>$I_{sc}$ [mA]</th>
<th>$V_{oc}$ [mV]</th>
<th>$R_{sh}$ [Ω]</th>
<th>$R_{p}$ [Ω]</th>
<th>$P_{max}$ [W]</th>
<th>FF</th>
<th>$E_{st}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz-Si (100) – regular piramidal texture</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>150</td>
<td>869</td>
<td>599</td>
<td>10.25</td>
<td>16.4</td>
<td>374</td>
<td>0.719</td>
<td>14.92</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>870</td>
<td>600</td>
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<td>15.1</td>
<td>384</td>
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<tr>
<td>3</td>
<td>250</td>
<td>873</td>
<td>601</td>
<td>36.68</td>
<td>17.4</td>
<td>393</td>
<td>0.749</td>
<td>15.68</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>872</td>
<td>601</td>
<td>32.26</td>
<td>18.1</td>
<td>391</td>
<td>0.746</td>
<td>15.60</td>
</tr>
<tr>
<td>5</td>
<td>320</td>
<td>846</td>
<td>599</td>
<td>48.60</td>
<td>19.8</td>
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<td>0.767</td>
<td>15.50</td>
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<tr>
<td>6</td>
<td>400</td>
<td>837</td>
<td>597</td>
<td>55.04</td>
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<td>0.765</td>
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</tr>
<tr>
<td>mc-Si – random geometrical figures texture</td>
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<tr>
<td>7</td>
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<td>580</td>
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<td>293</td>
<td>0.665</td>
<td>11.67</td>
</tr>
<tr>
<td>9</td>
<td>250</td>
<td>752</td>
<td>580</td>
<td>16.67</td>
<td>18.2</td>
<td>295</td>
<td>0.676</td>
<td>11.76</td>
</tr>
<tr>
<td>10</td>
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<td>39.4</td>
<td>297</td>
<td>0.704</td>
<td>11.65</td>
</tr>
</tbody>
</table>

where: $I_{sc}$ – short circuit current, $V_{oc}$ – open circuit voltage, $R_{sh}$ – shunt resistance, $R_{p}$ – series resistance, $P_{max}$ – power in optimum point, FF – fill factor, $E_{st}$ – conversion efficiency.

The cells numbered from 1 to 6 have homogenous surface texture presented in Fig. 2a. For the cells numbered from 7 to 12 only one example of the surface texture is presented in Fig. 2b due to random crystallographic orientation of the particular grains.

The present results indicate that the electrical parameters of the silicon solar cell depend on the temperature of the TiO₂ deposition. The CVD process performed at 250°C leads to the best photoconversion efficiency. For the lower deposition temperature of TiO₂, the obtained $V_{oc}$ and $R_{sh}$ values suggest, that the TiO₂ layer does not protect effectively p-n junction from penetration of silver atoms. However, above 250°C, the presence of the crystalline phase of anatase (as shown in Fig. 3) makes the metallization process more difficult which results in the lowering $I_{sc}$ and increasing $R_{sh}$ values and consequently leads to the photoconversion efficiency decrease.

5. Conclusions

The evolution of the crystallographic structure with the substrate temperature for the TiO₂ layers containing anatase phase embedded in the amorphous background has been shown. A progress of the crystallization process with the increasing temperature of the substrate during the TiO₂ deposition by CVD method has been observed. The process performed at 250°C leads to the best photoconversion efficiency. This is a compromise between protection and antireflection role of TiO₂ layer in silicon solar cell structure. The effect is the same for the monocrystalline silicon solar cells with regular piramidal texture of the surface and for the multicrystalline silicon solar cells with random geometrical figures texture. From an optical point of view the best antireflection properties has the TiO₂ layer deposited at 400°C, with $k$ coefficient near to zero.

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REFERENCES


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