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Invited Paper

In situ spectroscopic ellipsometry study of low-temperature epitaxial silicon growth

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ABSTRACT

Low-temperature growth of doped epitaxial silicon layers is a promising way to reduce the cost of p-n junction formation in c-Si solar cells. In this work, we study process of highly doped epitaxial silicon layer growth using in situ spectroscopic ellipsometry. The film was deposited by plasma-enhanced chemical vapor deposition (PECVD) on a crystalline silicon substrate at a low substrate temperature of 200 °C. In the deposition process, SiF_4 was used as a precursor, B_2H_6 as doping gas, and a hydrogen/argon mixture as carrier gas. A spectroscopic ellipsometer with a wide spectral range was used for in situ spectroscopic measurements. Since the temperature during process is 200 °C, the optical functions of silicon differ from these at room temperature and have to be adjusted. Thickness of the epitaxial silicon layer was fitted on in situ ellipsometric data. As a result we were able to determine the dynamics of epitaxial layer growth, namely initial layer formation time and epitaxial growth rate. This study opens new perspectives in understanding and monitoring the epitaxial silicon deposition processes as the model fitting can be applied directly during the growth.

1. Introduction

Upon almost three decades the epitaxial growth of thin silicon layers on crystalline silicon (c-Si) wafers have been intensively studied using different techniques [1–4]. Since there are various techniques of the epitaxial silicon (epi-Si) thin film fabrication, the most reported are the high temperature (650–1100 °C) chemical vapor deposition [1], the rapid thermal growth epitaxy [2], low-pressure chemical vapor deposition [3], and high vacuum electron-cyclotron-resonance plasma deposition [4]. During last years the plasma enhanced chemical vapor deposition (PECVD) technique plays an important role in research of epi-Si growth for its low-temperature deposition (as low as 150 °C) and without requirement of ultrahigh vacuum (UHV) systems [5].

In PECVD growth of epi-Si, gas precursors are used for the growth. Therefore it is easy and inexpensive to introduce and control doping of the grown layer. The epitaxial p-doped silicon films from $SiF_4/B_2H_6/H_2/Ar$ gas mixture were for the first time prepared by low temperature epitaxy by Leal et al. [6–8]. Compared to other techniques, the main advantage of the PECVD process is that it provides easy control of thickness depth doping profile by adjusting doping gas flow and type during the process with the level of doping from intrinsic to a very high doping [9].

Because the growth rate of epi-Si is affected by a plasma conditions inside the PECVD reactor, it is necessary to observe the growth process in situ to be able to control the thickness of the epi-Si layer precisely. In situ spectroscopic ellipsometry was used because it is a non-destructive, high accuracy, and sensitivity optical method. By modeling and fitting of in situ spectroscopic ellipsometry (SE) data obtained in full spectral range we demonstrate benefits in model stability and epi-Si thickness evolution determination. This approach can extend previous SE studies of the low temperature PECVD epi-Si growth presented as a single-wavelength evolution of imaginary part of pseudo-dielectric function [10,11]. In this paper we present first in-situ study of the low temperature PECVD growth of the p-doped epi-Si.

In the next sections we will describe details of the p-doped epi-Si layer growth and describe principles of the in situ SE measurement. The paper ends with an analysis of the dynamics of the epi-Si layer growth during the low temperature PECVD process.

2. Sample preparation and in situ ellipsometry

2.1. Growth of the epitaxial silicon layer

An epitaxial silicon layer has been grown for 60 min in a PECVD

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reactor designed for 5 in. size wafers. The reactor is part of a cluster tool for solar cells fabrication. This is a symmetric capacitively coupled radio-frequency (13.56 MHz) PECVD reactor composed of a shower head on the RF electrode and a grounded electrode used as the substrate holder. The inter-electrode distance was 20 mm. Both the RF electrode temperature and the substrate temperature were set at 200 °C. The RF power density was fixed at 180 mW/cm^2 and the working pressure was set at 2.5 Torr, while SiF_4 and Ar flow rates were respectively fixed at 20 and 300 sccm. Such a high Ar flow rate is associated with a higher dissociation of SiF_4. The diborane (B_2H_6) flow rate was 1 sccm. Diborane was diluted in hydrogen; its concentration in the gas cylinder is 0.9%.

The n-type float-zone (FZ) ⟨100⟩ c-Si wafer (with a resistivity of 1–5 Ω cm) were used as substrates. Before loading to the reactor it was cleaned using a 5% HF bath during 30 s to remove the native oxide.

2.2. In situ spectroscopic ellipsometry

Growth of the epitaxial silicon layer was measured with an in situ spectroscopic ellipsometer (SE) Woollam M-2000DI with spectral a range from 0.73 eV to 6.42 eV (193–1700 nm). A halogen bulb and deuterium lamp are used for sample illumination. After light reflection from the sample the spectral dependence of ellipsometric parameters is achieved using diffraction grating and CCD array as detector. Therefore all spectral points are measured at the same time. The total acquisition time for one spectrum acquisition was 3 s with 10 s delay between SE measurements. The SE data were measured continuously for 78.2 min, i.e. 10.5 min before the plasma process, 60 min during epi-Si growth, and 7.7 min after plasma switch off. During the process, 690 full SE spectra were recorded. The angle of incidence of the in situ ellipsometer was 70.9° and 1 zone measurement with fixed azimuthal angle of 45° for polarizer and continuously rotating compensator was used. For optical system without depolarizations and measurable conversion between TE and TM modes, the measured ellipsometric quantities N, C, and S are components of normalized reflection Mueller matrix [12,13]:

$$\mathrm{M} = \begin{bmatrix} 1 & -N & 0 & 0 \\ -N & 1 & 0 & 0 \\ 0 & 0 & C & -S \\ 0 & 0 & S & C \end{bmatrix}. \tag{1}$$

The Mueller matrix (1) is normalized by the element M_{11}, which describes the total reflected intensity of unpolarized light. The elements N, C, and S are related to the classical ellipsometric angles ψ and Δ as follows:

$$N = \cos 2\psi, \quad C = \sin 2\psi \cos \Delta, \quad S = \sin 2\psi \sin \Delta. \tag{2}$$

Ellipsometric angles ψ and Δ represent relative phase and amplitude of the ratio of complex reflection coefficient:

$$\frac{r_{\mathrm{pp}}}{r_{\mathrm{ss}}} = \tan \psi e^{i\Delta}. \tag{3}$$

Fig. 1 shows in situ measured spectra of ellipsometric parameters N, C, and S as a function of time. During epi-Si layer deposition process, the data clearly show interference fringes in NIR region and increasing of their frequency with increasing processing time.

In the SE data analysis, the Leverberg–Marquard least-square minimization algorithm was used [14]. The following merit function χ^2 was used as a criteria for the model fit of a single spectra:

$$\chi^2 = \frac{1}{3K - L - 1}\left[\sum_{k=1}^{K} \frac{\sum_{X\in\{N,C,S\}} (X_k^{\mathrm{meas.}} - X_k^{\mathrm{mod.}})^2}{\sigma_k^2}\right], \tag{4}$$

where N, C, and S are ellipsometric quantities defined by Eq. (2). Superscripts *meas.* and *mod.* stands for measured and modeled data, respectively. Value of the estimated measurement error $\sigma_k = 0.001$ was used for all models and spectral points to acquire comparable values of merit function. K is the number of spectral points (710 in this case), and L is the number of fitted parameters.

3. Results and discussion

To determine the evolution of the epitaxial layer thickness, i.e. the growth rate of the epi-Si, all the SE data were fitted with a model consisting of the c-Si substrate, hydrogenated Si interface layer, epi-Si layer, and surface roughness. The layout of the structure used for data fit is shown schematically in Fig. 2.

The thickness of the epitaxial Si layer was assumed to be the only fitting parameter. In the model, the hydrogenated silicon interface and surface roughness were approximated as a layer with effective permittivity corresponding to mixture of c-Si and void ($\epsilon = 1$). Permittivity was calculated using Bruggeman effective medium approximation (BEMA) with fixed volume fraction $f = 0.5$ [15]. The volume fraction was fixed to eliminate its correlation with the effective medium layer thickness (below 1 nm). In the first step of data analysis the fitted thicknesses of effective medium layers showed small variations, less than 0.2 nm, during the plasma process. Therefore, in the second step of the analysis, the thickness of the hydrogenated interface was fixed in the model to $t_{\mathrm{H-Si,BEMA}} = 0.8$ nm and the surface roughness was fixed to $t_{\mathrm{rough.,BEMA}} = 0.6$ nm. By this correlation between those two thicknesses was eliminated, which improved quality of the fit. The main benefit of the surface roughness layer was improvement of the quality of the fit in the UV region.

In the analysis of the in situ ellipsometric data, it is important to take into account the influence of deposition conditions to in situ SE measurements. In our process, the permittivity of the silicon used in the model is affected by temperature (200 °C) during the fabrication process. To demonstrate this effect, we compare two models. In the first model, the optical function of crystalline silicon at room temperature (RT) determined by Herzinger et al. [16] was used. The second model was improved with optical function of c-Si parameterized for 200 °C. The permittivity data was exported from Woollam CompleteEASE software using provided model *Si Temp JAW (Temp Library).mat*. Fig. 3 shows optical function of crystalline silicon at RT and 200 °C, respectively. Subplot clearly shows a red shift of the absorption peaks and change of amplitudes with temperature.

Fig. 4 shows the result of fit of the ellipsometric parameter S with the model based on RT and 200 °C c-Si permittivity. In transparent region, for photon energies below 2.8 eV, both models can describe interference fringes. Therefore, both are sensitive to the change of the epi-Si thickness. On the other hand, RT c-Si based model (Fig. 4, subplot (a)) does not fit well in the high absorption region, at c-Si major absorption peaks positioned at 3.4 eV and 4.2 eV, respectively. The 200 °C c-Si optical function in model [Fig. 4, subplot (b)] improves the fit significantly and gives a very good agreement over the whole measured spectral region. Improvement of the fit is directly related to the decrease of c-Si absorption peaks and their slight red-shift with increased temperature.

By fitting of all measured spectra sequentially, a time-evolution of the epi-Si layer thickness was determined. Fig. 5 shows thickness evolution obtained for both c-Si optical functions discussed previously. The PECVD process, starting at $t = 10.5$ min and finishing at $t = 70.6$ min is highlighted by the blue box. As we have discussed, both models gave comparable agreement at NIR region with interference fringes, therefore both can describe time-evolution of the thickness. The subplot (a) of Fig. 5 shows smooth constant growth between 17.6 min and 51.5 min of deposition and ends at comparable thickness: 305 nm for RT, 300 nm for 200 °C permittivity, respectively. The time frame of the constant growth rate is marked with vertical dash-dotted lines. Although the constant growth rate is similar for both optical functions of c-Si within this time frame, the model with RT c-Si optical functions gives worse sensitivity to the epi-Si film thickness in the beginning of the process. Therefore, room temperature c-Si functions lead to an initial