Porous silicon Bragg reflectors on multi-crystalline silicon wafer with p-n junction

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Abstract. Bragg reflectors consisting of the sequence of dielectric layers are considered to create p-n junction solar cells (SC) with improved efficiency in the longwave spectral range. Bragg mirrors (BM) based on porous silicon (PS) multilayers at the backside of single crystalline and multicrystalline silicon wafer were formed by electrochemically etching. Maximal experimental reflectivity for BM on multicrystalline substrate achieves 62% due to the natural crystallites disorientation of multicrystalline substrate, whereas for single crystalline silicon the reflectivity in maximum is 87%. BM was formed also on rear side of multicrystalline silicon wafer with p-n junction.

1. Introduction
The increasing efficiency of SC and the reducing their cost is the main direction of development of solar energy through direct conversion of solar energy into electricity. The concept of third generation solar cells declares the need to improve the efficiency of existing SC using new technology opportunities and the creation of SC that operate on new principles [1]. Process parameters and production phases optimization of existing designs of silicon SC is realized to implement this concept. SC with quantum wells [2] and quantum dots [3], organic material [4] and dyes based dispersed SC [5], thin film SC [6] are actively investigated.

There are some main power losses mechanisms for single p-n junction SC [7]. The first one is due to thermalisation losses of photogenerated charge carriers. The second one is inability of SC to absorb the photons with energies less than the semiconductor band gap. The cost of commercial Si SC can be decreased at the using of thinner wafer. However, it results in the reduction of absorption of low energy photons. One of the way to overcome this problem is the modification of SC design with the improved schema of photons trapping having absorption length $L \cdot \alpha=1/\alpha>L_w$ (figure 1), where $\alpha$ is absorption coefficient of semiconductor wafer, $L_w$ is wafer thickness.
Pyramids texturing [8] and antireflection layers [9] are used to reduce reflection from front SC. Photon traps [10], rear reflectors [11] and texturing [8] are used to increase photon effective absorption length due to multiple reflections of photons inside wafer.

PS as Si-technology compatible material can be used to form antireflection coating and rear reflector for Si SC [12]. PS is grown by electrochemical etching from crystalline Si in electrolytes containing hydrofluoric acid (HF) [13]. PS layer parameters are depended on etching current density, etching time, solution composition and wafer crystal-lattice orientation. PS rear reflector is used as a base for further deposition of thin film SC by epitaxy or chemical vapor deposition [14]. Modern commercial SC are fabricated on the base of single crystalline as well as multicrystalline Si wafers, so spectral dependences of reflectivity for single and multicrystalline Si based reflectors have to be different due to porosity dependence on crystal-lattice orientations [15].

In present work we consider structures with rear PS Bragg mirrors on single crystalline and multicrystalline silicon substrates and propose the method to fabricate PS Bragg mirror on two-side textured multicrystalline silicon wafer with formed p-n junction.

2. Experiment

Bragg mirror can be used as a rear reflector for multi-passing of IR photons within the SC. BM has high reflectivity within certain spectral range (figure 1). BM is a structure formed from multiple layers of alternating materials with different refraction indexes. In simple case BM is the stack of two layers with optical thicknesses $n_l l_l = n_h l_h = \lambda_0 / 4$, where $\lambda_0$ is the wavelength of BM maximum of reflection, $n_h$, $n_l$ are refraction indexes of layers, $l_h$, $l_l$ are thicknesses of layers [16].

Bragg mirrors were fabricated by electrochemical etching of single- and multi-crystalline p-type silicon wafer. Electrochemical treatments were in HF/C$_2$H$_5$OH solution mixed in the ratio 4:1. Diameter of all samples is 2.5 cm, area is 4.9 cm$^2$. “Step-like” current treatment profile with sharp current values changes was used.

All measurements of reflection coefficients were performed using standard reflectivity measurement system consisting of a light source, computer controlled monochromator, chopper, Si-photodiode as light sensor, selective multimeter, ADC board. Measurements were performed in dark room in isolated black box. Reflection coefficients were measured using integrating sphere to take into account diffuse component of reflected light. Certified samples with known spectral reflectivity dependence were used for measurement system calibration before every measurement of reflection coefficient.
Reflection coefficient of BM on 2-side polished single crystalline silicon wafer are $R_{\text{max}}^{1}(\lambda_0 = 788 \text{ nm}) = 86.5\%$ (figure 2, curve I). Etching parameters and obtained refraction indexes were the following: $j_{\text{H}} = 1.8 \text{ mA/cm}^2$, $n_{\text{H}} = 2.1$; $j_{\text{L}} = 623 \text{ mA/cm}^2$, $n_{\text{L}} = 1.4$. Reflection coefficient of BM on 2-side polished multicrystalline silicon wafer are $R_{\text{max}}^{2}(\lambda_0 = 840 \text{ nm}) = 61.8\%$ (figure 2, curve II).

In the vicinity of Bragg peak (BP) the reflection coefficients of BMs fabricated on mono- and multi-Si is larger than reflection coefficients of mono- and multi-Si wafer (figure 2, curve III and IV respectively). Multicrystalline silicon wafer consists of elementary clusters with different crystal-lattice orientation. So, due to dependence of growth rate of PS layers on crystal lattice orientation, effective total reflection coefficient of such BM is defined as weighted sum of reflection coefficients of separate elementary clusters as well as clusters’ area.

To fabricate BM on multicrystalline silicon wafer such etching parameters as growth rate $\nu_{PS}(j)$ and refraction index $n(j)$ were taken for crystal lattice orientation $<100>$. Crystal lattice orientation within elemental cluster and area of cluster varies from wafer to wafer and, therefore, total reflection coefficient of multicrystalline based BM is less than for single crystalline based BM: $R_{\text{max}}^{2} < R_{\text{max}}^{1}$. Such BM can be used as base to fabricate SC with rear reflector. SC can be formed on the top of BM using such technologies as chemical vapor deposition, molecular-beam epitaxy.

BM formed on both-side textured structure with formed p-n junction was formed. Wafer parameters are the following: wafer thickness 200 $\mu$m ($N_{\text{d}} = 10^{16} \text{ cm}^{-3}$), phosphorus doped ($N_{\text{d}} = 10^{20} \text{ cm}^{-3}$) emitter thickness is 300 nm, sample area is 4.9 $\text{cm}^2$. Alternative current profile was used for electrochemical treatment (figure 3, insert). BM has to be formed on external base interface, so structure with p-n junction is under reverse bias condition for traditional “step-like” current treatment profile and, therefore, alternative current profile was used to grow BM. Alternative current treatment frequency was 100 Hz. Treatment amplitudes $I_L$ and $I_H$ ($j_{\text{L}} = 10 \text{ mA/cm}^2$, $j_{\text{H}} = 348 \text{ mA/cm}^2$) were chosen to obtain required PS layers growth rates and refraction indexes ($n_{\text{H}} = 1.9$, $n_{\text{L}} = 1.6$). Treatment parameters $j_{\text{H}}, j_{\text{L}}, t_{\text{H}}, t_{\text{L}}$ were chosen to obtain BP maximum at $\lambda_0^{3} = 570 \text{ nm}$. Measured reflection coefficient is $R_{\text{max}}^{3}(\lambda_0^{3} = 572 \text{ nm}) = 32.4\%$ (figure 3).

**Figure 2.** Experimental spectral dependences of reflection of BM grown on single crystalline p-Si ($<100>$ orientation) both-side polished wafer $\lambda_0 = 788 \text{ nm}$ (curve I), BM grown on multicrystalline p-Si wafer $\lambda_0 = 840 \text{ nm}$ (curve II), single crystalline p-Si ($<100>$ orientation) both-side polished wafer (curve III), multicrystalline p-Si wafer (curve IV).
BP shape (figure 3, curve I) is worse comparatively to shape of BP of Bragg mirrors (figure 2) formed on single- and multicrystalline both-side polished Si wafer. It can be explained by rear contact interface roughness due texturing. Wafer with preliminarily formed texture has not flat contact with electrode during electrochemical treatment, non-uniform PS layer growth is observed. The spectral dependence of reflectivity before PS forming is shown in figure 3 (curve II). The curve of reflection coefficient for structure with BM lies above than for structure without BM. Electrochemical treatment of textured wafer with existing p-n junction is complicated process and requires additional optimization.

The elaborated structures with porous silicon BM show high stability and reversibility. Particularly, the 30 min annealing at 900°C did not change the optical parameters of structures.

3. Conclusion

Bragg reflector on the base of porous silicon can increase absorption of IR photons due to multi-passing IR photons and properly absorption length increasing inside monocrystalline and multicrystalline Si wafer. Electrochemical treatment with sharp “step-like” current treatment profile can be used to fabricate BM with maximum measured reflectivity 86% for monocrystalline Si wafer and 61% for multicrystalline Si wafer. Total reflectivity of multicrystalline Si wafer is defined by weighted sum of reflection coefficients of separate elementary wafer clusters. BM can be formed on structure with formed p-n junction using alternative current treatment profile.

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