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The influence of chemical pretreatment on the passivation efficiency of textured silicon wafers

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The influence of the chemical surface pretreatment by the RCA (Radio Corporation of America) and modified Shiraki methods prior to passivating with a layer of amorphous hydrogenated silicon on the effective charge-carrier lifetime was investigated. The effect was studied on silicon wafers textured by various etching methods, including inductively coupled plasma reactive ion etching and wet etching. The preference of the modified Shiraki method was demonstrated. The maximum achieved value of the effective carrier lifetime for wafers textured by reactive ion etching with inductively coupled plasma was 400 μs, while that for wafers textured by the combined wet/RIE method was 500 μs.

Keywords: photovoltaic converters, silicon, amorphous silicon, black silicon, passivation, reactive ion etching.

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A topical problem of solar power engineering is recombination of nonequilibrium charge carriers on solar cell defects. Passivation of the silicon wafer surfaces leads to attenuation of the carriers recombination on surface states and, hence, to an increase in the efficiency of solar radiation conversion. On the other hand, efficiency of a solar cell based on crystalline silicon can be increased by surface texturing which leads to a decrease in the reflected light fraction. One of the most efficient methods for texturing silicon is creating on its surface nanofibers, i.e. the so-called „black silicon“. Black silicon (b-Si) obtainable by reactive ion etching combines antireflection properties in a wide range of wavelengths (400–1150 nm) and ability to optically absorb poorly absorbable photons with energies close to the silicon absorption edge [1–3]. However, texturing enlarges the effective interface area due to which the effect of surface states gets enhanced. In this study, we investigated the effect of chemical pretreatment prior to passivating the surfaces of textured silicon wafers on the effective lifetime of nonequilibrium charge carriers (τ_{eff}). Determination of τ_{eff} by measuring the photoluminescence decay (PLD) kinetics with chart construction (Fig. 1) allows estimating the level of surface recombination [4].

Passivation was performed by depositing an undoped a-Si:H(i) layer which provided the lowest concentration of the silicon surface defects [5]. In this work, n-type (100) silicon wafers with resistivity of $1-5\,\Omega\cdot$cm were used. The study was carried out on textured silicon wafers grown by the Czochralski method and having a bulk lifetime of at least 2 ms. Wafers of the following types were used: a non-polished silicon wafer after slicing (AS-Si), and a silicon wafer with removed defective surface layer (SDR-Si). As a reference sample, there was used a double-side polished silicon wafer (DSP-Si Topsil PV-FZ) grown by the floating zone method and having bulk lifetime of at least 10 ms. Taken in various combinations, the wafers were subjected to the following technical processes: texturing in a potassium hydroxide solution (KOH, 80 s), reactive ion etching using an inductively coupled plasma source at the cryogenic (cryo-ICP RIE) and close-to-room (ICP RIE) temperatures. Etching by the cryo-ICP RIE method was conducted in the environment of gaseous sulfur hexafluoride, oxygen and argon (5 mTorr) at the temperature of -150°C and power of 1000 W for 2 min [6]. The ICP RIE etching was performed for 10 min at the pressure of 5 mTorr and power of 700 W. Prior to depositing the passivation layer, silicon wafers were treated in one of the following three ways: with an aqueous solution of hydrofluoric acid (HF, 10%), RCA (Radio Corporation of America) method (standard clean 1 — SC1, standard clean 2 — SC2) [7], or modified Shiraki method (CCl_4, HNO_3+RCA) [8] using isopropyl alcohol instead of methyl alcohol. After chemical

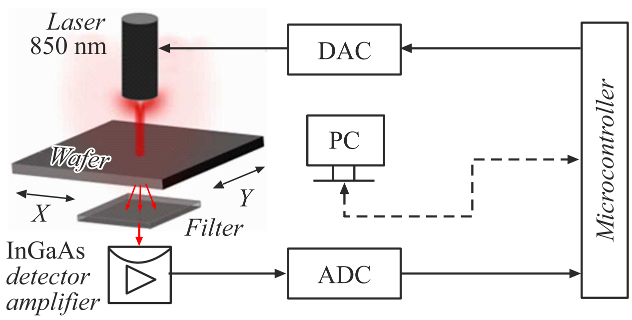

Figure 1. Experimental setup for measuring photoluminescence decay.

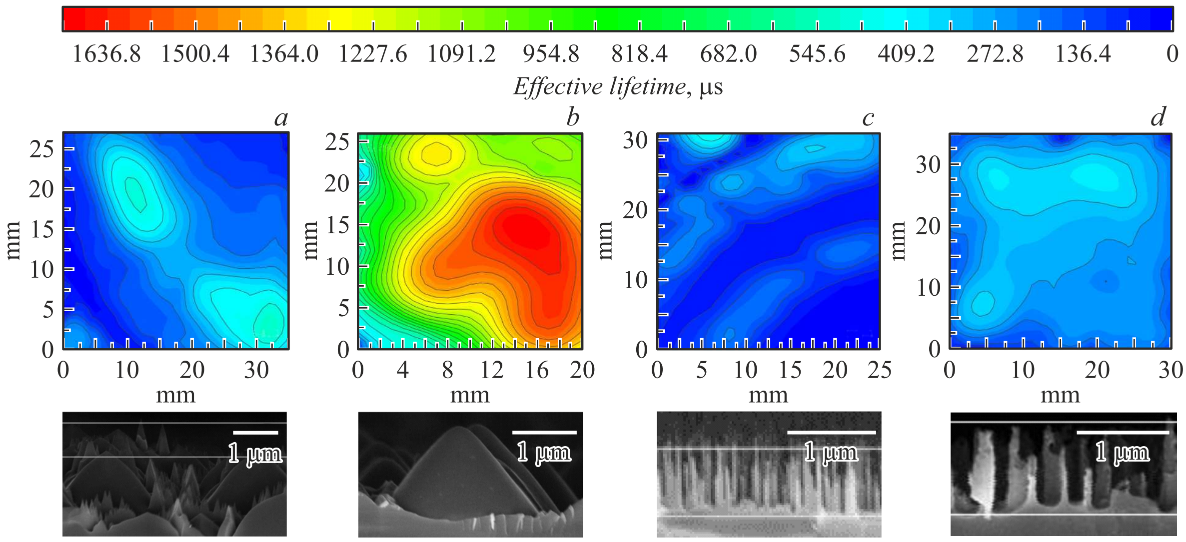

Figure 2. Charts of the maximum effective lifetime of nonequilibrium charge carriers and SEM images. *a* — AS-Si (KOH, cryo-ICP RIE, RCA), *b* — AS-Si (KOH, RCA), *c* — SDR-Si (cryo-ICP RIE, RCA), *d* — SDR-Si (ICP RIE, modified Shiraki method).

treatment, passivation of silicon wafers was performed at setup „Oxford Plasmalab System 100 PECVD“ in the way of plasma-chemical deposition (PECVD) of an amorphous silicon layer (a-Si:H) 40 nm thick. Deposition was carried out at the temperature of 250°C, pressure of 350 mTorr, and high-frequency plasma power (13.56 MHz) of 11 mW/cm^2; the deposition speed was 8 nm/min. Monosilane (SiH_4) was used as a precursor for the a-Si:H deposition.

Fig. 2 presents the τ_{eff} distribution charts and scanning electron microscope (SEM) surface images for textured samples. The obtained charts (Fig. 2) demonstrate nonuniformity of the τ_{eff} distribution. The edge effects are explained by nonuniformity of the PECVD deposition of the passivation layer [9]. In addition, the sample cleavage increases the concentration of defects. Nonuniformity of the τ_{eff} distribution in the center of the sample is explained by differences in the post-texturing morphologies. Depending on the texturing mode and method, areas with different fiber densities get formed on the wafers, which also affects τ_{eff}. The fiber height is indicated in the SEM images (Fig. 2) with a light line.

The maximum τ_{eff} values obtained for wafers subjected to various chemical-cleaning and surface-texturing methods are presented in the Table. First the chemical treatment effect was estimated for a series of reference samples (DSP-Si) in which, on the one hand, the modified Shiraki method provided the best result, but, on the other hand, the difference ranged within 20%. In view of a large number of samples, as well as of high resource consumption of the RCA and Shiraki methods, these methods were applied not for all texturing types. When τ_{eff} was very low (less than 10 μs) or already quite high (0.5 ms), the Shiraki method was not applied. The Table shows that τ_{eff} values of textured silicon wafers after wet chemical etching are higher than those of silicon wafers with partially removed defective layers but lower than those of polished wafers, which agrees well with literature data [10].

Treatment with the RCA method gives better results than HF treatment in all the considered cases. In the case of plasma etching (cryo-ICP RIE) of the AS-Si substrates, assessing the effect of chemical pretreatment turns to be impossible because of too low τ_{eff} values caused by high defect concentration in the surface layer. Unlike wet etching, dry plasma etching does not allow removing the layer damaged in the process of slicing the ingot into wafers. When the cryo-ICP RIE method is used, etching depth of the AS-Si substrates is about 900 nm (Fig. 2, *a*). This means that plasma etching is to be applied to substrates with pre-removed damaged layers (SDR-Si). It was found that in this case the modified Shiraki cleaning procedure provides better passivation quality for silicon wafer surfaces subjected to ion etching than that provided by the RCA method. At the same time, for the SDR-Si silicon wafers subjected to reactive ion etching by the ICP RIE method, τ_{eff} values of about 0.4 ms were achieved, which demonstrates good passivation quality (Fig. 2, *d*) despite rough nanofiber surfaces. Notice that the cryo-ICP RIE method provides significantly lower τ_{eff}. Heights of fibers obtained on the SDR-Si substrates by the cryo-ICP RIE (790 nm) and ICP RIE (770 nm) methods differ only slightly (Fig. 2, *c*, *d* /); however, in the first case the fiber density is significantly higher, which is just what determines the observed difference in the τ_{eff} values, since the higher is the fiber density, the greater is the surface state concentration.

Thus, the study has shown that texturing of wafers by wet chemical etching may be performed directly after slicing the ingot (AS-Si). Additional chemical treatment by the RCA method immediately before passivation ensures very high values of τ_{eff} (up to 1.7 ms). In the case of dry plasma etching it is necessary to use wafers with pre-

Measurements of maximum effective lifetime τ_{eff} τ_{eff}

№	Substrate type	Surface modification method	Maximum effective lifetime τ_{eff}, μs		
			HF	RCA	Modified Shiraki method
1	AS-Si	cryo-ICP RIE	Below 10	Below 10	–
2		KOH	500–800	1000–1700	–
3		KOH, cryo-ICP RIE	100–250	200–500	–
4	SDR-Si	–	200–600	–	–
5		cryo-ICP RIE	–	15–60	20–70
6		ICP RIE	–	–	300–400
7	DSP-Si	–	2300	2700	2900

removed damaged layers (SDR-Si). Additional cleaning by the modified Shiraki method prior to passivation allows obtaining the maximum τ_{eff} values. After optimizing the technological process, the maximum value $\tau_{eff} = 400\,\mu$s was reached for black silicon wafers with highly developed surfaces (SDR-Si etched by ICP RIE).

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Conflict of interests

The authors declare that they have no conflict of interests.

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