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Influence of low-energy ion-beam treatment by hydrogen on electrical activity of grain boundaries in polycrystalline silicon

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Abstract

The results of investigation into the effect of hydrogen plasma treatment and annealing on the electrical activity of grain boundaries (GBs) in silicon ribbons manufactured with the edge-defined film-fed growth (EFG) technique are presented. It is shown that hydrogenation with small doses of introduced hydrogen leads to decrease of the GB electrical activity, whereas further growth of hydrogenation time gives rise either to saturation or increase of electrical activity for annealed and non-annealed ribbons, respectively. The latter is explained in terms of a model taking into account the concurrence of GB defects passivation and neutralization of boron ions in the vicinity of GB during hydrogenation.

Keywords: EFG silicon; Grain boundaries; Electrical activity; Hydrogenation

1. Introduction

As is known, grain boundaries (GBs) and dislocations are the most essential types of extended defects determining electrical properties of polycrystalline silicon edge-defined film-fed growth (EFG) ribbons [1]. Their presence is the main barrier to a wider use of polycrystalline silicon as photovoltaic material [2]. Therefore, the development of different methods enabling one to suppress the electrical activity of extended defects is an important task for the present-day polysilicon materials science.

In this paper we have studied a possible reduction of electrical activity of GBs in EFG silicon using heat treatment of as-grown ribbons by different regimes and in different ambients, and hydrogen plasma treatment both for as-grown and annealed polycrystals.

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2. Experimental

Boron-doped 1–3 Ω cm EFG silicon represented by hexahedral thin-walled hollow crystals 0.4–0.8 mm thick [3,4] has been studied. Note that the studied ribbons were characterized by the large-grain structure with grain dimensions of about 0.5–1.0 cm. This has allowed investigation of every individual grain boundary using structural and electrical characterization. All GBs in the studied as-grown ribbons have been subjected to a special X-ray diffraction (XRD) analysis that allowed nomenclature for every GB by the value of reciprocal density of coincident sites (Σ) at the GB plane that is the main crystallographic parameter of certified GBs. As has been shown by XRD, most GBs in the studied ribbons could be classified as weakly deviated from special orientations Σ 3, 9 [3,4]. Before electrical characterization, the as-grown ribbons were cut into a system of parallel rectangular samples containing a number of identical GBs. This made it possible to prepare individual electric probes for every GB so as to study their electrical activity depending on the crystallographic type and treatment regimes.

In our experiments we have studied the ribbons in two states—original (as-grown) and annealed in vacuum at 1100 °C during 2 h. The samples studied were subjected to hydrogen plasma treatment over the temperature range from 30 to 200 °C with the energy of hydrogen ions 100–500 eV and ion current density $50-100\,\mu A/cm^2$.

The electrical activity of grain boundaries was estimated by measurements of transversal static current–voltage (I–V) characteristics over the temperature range 77–300 K and by using the light beam-induced current (LBIC) regime according to the scheme presented in Fig. 1. The mechanism of the detected signal formation with such an LBIC technique can be explicated in the following manner [5]. During scanning of polycrystals by a narrow laser beam, the generation of the minority carriers takes place. When an electron–hole pair is generated in the space charge region (SCR) around GB (or another extended defect) or within the diffusion length from it, under the action of the electrical field of SCR, the minority carriers (electrons, in our case) can reach GB and recombine with the holes captured by the GB defects. Being transformed into the neutral state, the latter capture holes from the neighboring grains giving rise to some recombination current in the closed circuit. When an additional bias voltage is applied to the sample, the electron–hole pairs generated by a laser beam lead to the appearance of an additional current determined by thermal emission of the majority carriers over the potential barrier reduced due to the minority carriers capture.

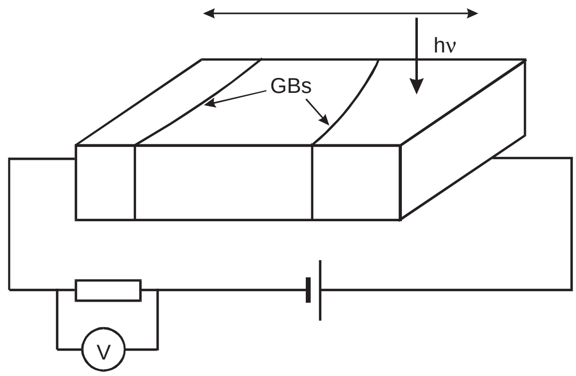

Fig. 1. Sketch of the scheme used for LBIC measurements.

It is obvious that a value of the charge localized at GB, the width of SCR and hence the probability that GB may be reached by the generated minority carriers are proportional to each other. Thus, we can state that the intensity of the beam-induced current correlates with the electrical activity of GBs.

As is seen from Fig. 1, in our experimental setup for LBIC measurements the studied sample has been series resistor connected to the DC source. With illumination of the sample by modulated monochromatic light (wavelength of 630 nm), the voltage across the series resistor was recorded by a selective voltmeter tuned to the modulation frequency. The spatial resolution of the method was defined mainly by mechanism of the scanning laser beam positioning that was about 20 μm. It was enough for resolution of individual GBs in the investigated ribbons with the large-grained structure. Correlation between the obtained photoresponse distributions, states of the ribbons structure and types of GBs enables one to analyze