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Effect of Sc and Yb Doping on Electrical and Luminescence Properties of Silicon Produced by the Stockbarger Method

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Abstract—The effect of scandium and ytterbium doping on the electrical and luminescence properties of polycrystalline silicon produced by the Stockbarger method was studied. It is found that the resistivity, the lifetime of minority charge carriers, and the position of the maximum of the low-temperature luminescence band, which are constant along the growth direction for undoped ingots, vary monotonically along the growth direction for doped ingots. Analysis of the photoluminescence spectra and conductivity in different parts of the doped ingots shows that variations in their electrical properties along the growth direction are due to a redistribution of background acceptors, whose concentration decreases steadily from the beginning of an ingot toward its end. The redistribution of the background impurities is related to the formation of background-impurity–doping impurity compounds, for which the distribution coefficients significantly deviate from unity in a silicon melt.

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1. INTRODUCTION

The most promising (from the points of view of ecological safety and nature equilibrium) kind of renewable energy sources is solar radiation energy, which can be directly conversed into electric energy. Mass production and employment of solar energy systems require creation of technologies and materials that would significantly reduce the cost of solar cells. It runs out that the fundamental limit for reduction of the cost of silicon solar cells, the base of solar energetics, is presented by high cost of silicon, the main source of which at present comes from scraps of high-purity silicon from microelectronic industry. Recently, we have demonstrated that widely available metallurgical-grade silicon obtained from high-purity silica can be used to produce cheap polysilicon for use in solar cells using directional recrystallization by the Stockbarger method [1]. Using this method, it is possible to clean out background impurities having a small distribution coefficient K in silicon melt.

However, the initial metallurgical-grade silicon contains not only impurities with low values of K but also impurities that have a distribution coefficient close to unity, for example, boron ($K = 0.8$). It seems that it is impossible to remove such impurities by directional recrystallization. In order to remove these impurities from silicon, we can use a well-known property of rare-earth elements, namely, its ability to "purify" a material when bulk crystals are grown using the Czochralski process or when epitaxial layers are deposited using liquid-phase epitaxy [2–7]. The mechanism of purification of semiconductor compounds during liquid phase epitaxy and Czochralski process with the addition of rare-earth elements in the melt involves the interaction of rare-earth elements with background impurities resulting in the formation of refractory chemical compounds, which remain in the melt as slag and do not penetrate into the growing film [5, 6]. In contrast to liquid phase epitaxy and Czochralski process, in a material grown using the Stockbarger method, the compounds formed by impurities with rare-earth elements are not separated into a phase external with respect to the grown material. However, the magnitudes of K of the compounds formed between impurities and rare-earth elements can significantly deviate from unity, which would lead to separation of the impurities during directional recrystallization.

In the present paper, we study the effect of doping by rare-earth element ytterbium and scandium, which is close to rare-earth elements in chemical properties, on the electrical and luminescence properties of metallurgical-grade silicon refined by Stockbarger-type directional recrystallization. It is demonstrated that doping

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† Deceased.

Fig. 1. Image of a typical polycrystalline silicon sample (fragment with dimensions 1.0 × 1.0 cm).

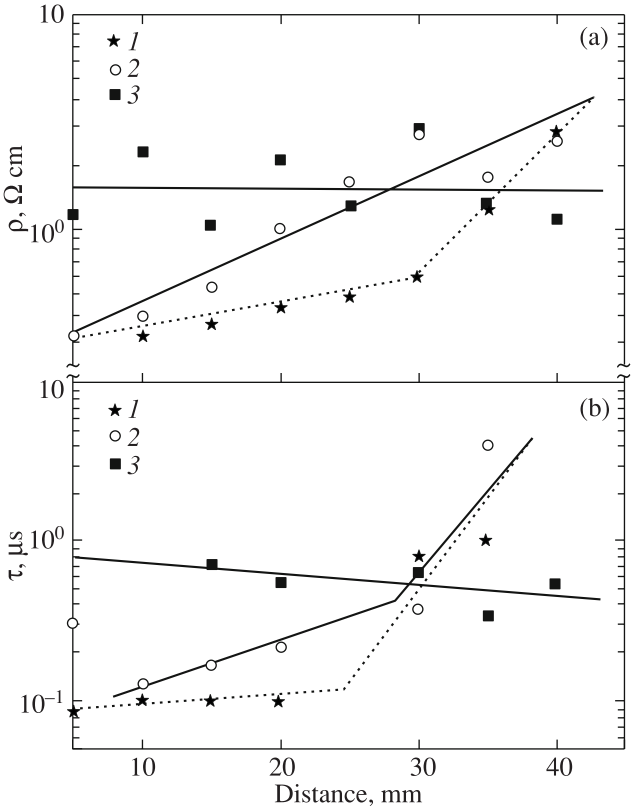

Fig. 2. Variations in (a) the resistivity and (b) carrier lifetime along the growth direction of ingots at T = 300 K: (*1*) Sc-doped and (*2*) Yb-doped samples and (*3*) the undoped sample.

by these elements causes a redistribution of background impurities along the growth direction of the ingot.

2. EXPERIMENTAL TECHNIQUE

The polysilicon samples studied in this work are grown using the Stockbarger method. The initial charge used is metallurgical-grade silicon specially produced in an MVA-25 ore-smelting furnace at Kremniĭ Closed Corporation (Shelekhov, Russia). The contents of the main impurities in the metallurgical-grade silicon can be found in [1]. We grew three 40-mm-long silicon ingots: undoped, scandium-doped, and ytterbium-doped ones. The concentrations of the dopants Sc and Yb are 5×10^{-4} atomic fraction. The process of ingot growth is described in detail in [8].

A typical fragment of a polysilicon ingot is shown in Fig. 1. In what follows, the part of a sample near the boundary between the ingot and the crucible is referred to as the "bottom" and the opposite side, as the "top" of the ingot. The polysilicon samples have grain sizes of at least 2–3 mm, straight intergrain boundaries, and, as we demonstrated in [8], a low density of growth dislocations (10^5–10^6 cm^{-2}) and have no other extended structure defects.

The obtained polysilicon samples are studied by electrical and optical methods. The resistivity ρ and the type of conductivity of samples are determined by the four-probe method. The lifetime of nonequilibrium charge carriers τ is determined from measuring photoconductivity decay in a contactless manner (using microwave power absorption) in the setup described in [9]. In the microwave measurements, nonequilibrium charge carriers are excited by an LPI-12 pulse semiconductor laser (pulse duration 0.125 μs). The quantities ρ and τ are measured at room temperature. Photoluminescence (PL) is excited by a He–Ne laser (λ = 632.8 nm) with a power density of 25 W/cm^2, analyzed by a double diffraction monochromator, and detected by a cooled germanium *p–i–n* diode (Edinburgh Instruments) using a lock-in technique. The measurements are carried out at T = 5 K.

3. RESULTS AND DISCUSSION

Figure 2 shows the resistivity and lifetime of nonequilibrium charge carriers measured along the ingots growth direction. It is clearly seen that, in the undoped sample, variations in ρ and τ along the growth direction are small. At the same time, in the Sc- and Yb-doped samples, ρ and τ change by more than an order of magnitude. Near the ingot bottom, these parameters are several times smaller and, near its top, they are several times greater than in the undoped sample. The undoped sample has *p*-type conductivity, and the conductivity of the doped samples changes from *p* type near the ingot bottom to *n* type near its top.

The low-temperature PL spectra of undoped, Yb-doped, and Sc-doped silicon ingots measured at various points along the growth direction are shown in Figs. 3a–3c. The spectra of the undoped silicon contain one broad band with a photon energy $h\nu$ ~ 0.99 eV at the

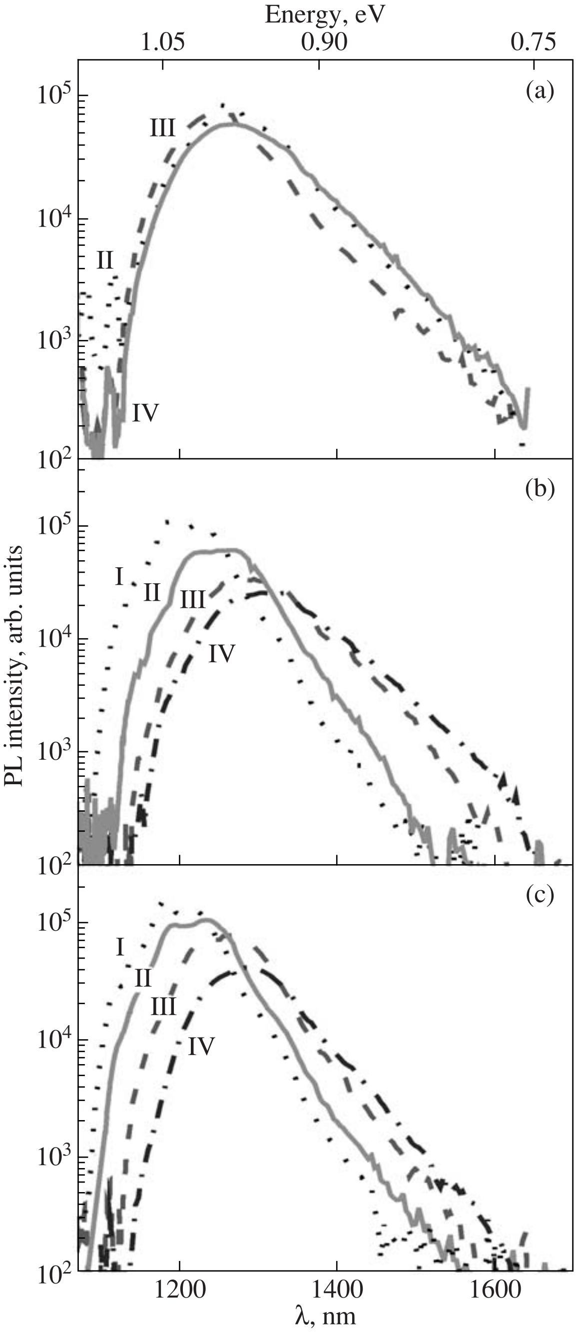

Fig. 3. PL spectra of (a) undoped, (b) Yb-doped, and (c) Sc-doped silicon samples measured at various points along the growth direction of the ingot at $T = 5$ K. The spectra are measured at the following distances from the ingot bottom: (I) 10, (II) 20, (III) 30, and (IV) 40 mm.

maximum and a full width at half-maximum (FWHM) $\Delta \sim 90$ meV. The magnitudes of $h\nu$ and Δ are almost independent of the measurement position. The observed spectra are typical of heavily doped materials [10]. The PL spectroscopic parameters of the doped silicon vary monotonically. Specifically, from the bottom of the ingot to its top, the position of the band maximum shifts toward lower energies and the width of the band increases. According to the data from [11], the low-energy shift of the PL band in heavily doped silicon is related to the shift of the Fermi level deeper into the tail in the density of states formed by acceptors because of the increasing degree of compensation of the material. The increase in the compensation in passing from the bottom to the top observed in the PL spectra of the ingot agrees well with the increase in the resistivity. The fact that the lifetime of nonequilibrium charge carriers increases simultaneously with resistivity indicates that the degree of compensation increases mainly due to the decrease in the concentration of acceptors and not to the increase in the concentration of donors. Note that long-wavelength PL appears in the PL spectra of the Yb-doped sample measured near the top of the ingot. It is due to recombination via deep centers related to defects and/or complexes formed by defects and background impurities. We believe that these defects are responsible for the different behavior of ρ and τ in Sc- and Yb-doped samples. The nature of the defects remains unknown at present, and further investigations are necessary to clarify it.

So, comparing the electrical and luminescence parameters measured in various points of the samples makes it possible to conclude that impurities in the undoped sample are distributed uniformly and that the addition of Sc and Yb creates a steady decrease in the acceptor concentration in passing from the bottom to the top of the ingot. We believe that the redistribution of the impurity in the doped samples occurs due to the formation of impurity–Sc and impurity–Yb complexes in the silicon melt for which the distribution coefficients *K* are much more different from unity than are the values of *K* for the background impurities.

4. CONCLUSIONS

In this paper, we have studied the effect of Sc and Yb doping on the electrical and luminescence properties of silicon produced by the Stockbarger method. It has been demonstrated that the doping causes a monotonic variation in the resistivity and lifetime of nonequilibrium charge carriers along the ingot growth direction and that the values of ρ and τ are several times larger (smaller) at the ingot bottom (top) than in the undoped material. The observed changes in the material parameters are explained by a redistribution of the concentration of background acceptors along the growth direction of the ingot due to the formation of compounds between a background impurity and the doping impurity, which have distribution coefficients in silicon melt differing significantly from unity.

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