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Study of Solar Silicon Multicrystals by SEM and EPMA Methods

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Abstract—Multisilicon crystals grown from refined metallurgical silicon are studied by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The varieties of intergranular boundaries are revealed. Impurities are found to be contained in inclusions in multisilicon. The intergranular boundaries contain no impurities, and they do not concentrate the elements present in multisilicon. It is proved experimentally that, in the homogeneous areas of the crystal the lifetime of minor charge carriers is maximum, whereas its minimum value corresponds to the areas with numerous intergranular boundaries.

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INTRODUCTION

Due to the rapid development of solar power, a colossal silicon deficit has arisen in world practice. Solution of this problem is now imperative and possible only with the use of alternative technologies that result in a substantial cost reduction for silicon production. One of the most promising areas is direct synthesis of multisilicon by targeted crystallization from high-purity refined metallurgical silicon obtained from especially pure natural quartzites [1]. Multisilicon obtained from refined metallurgical silicon has a more complex structure than does that of a superconductor because it contains different residual impurities. Purification of the material from impurities is considered to be a serious problem in crystal preparation. In order to improve the efficiency of multisilicon purification from impurities, targeted crystallization from the Bridgman–Stockbarger melt has been applied [1, 2].

The electrophysical properties of multisilicon are equally determined by distortions of the material crystal structure and the type and concentration of impurities, including where and how these impurities are located [2]. Studies of the composition of impurities and their distribution and concentration on different defects in the crystals provide, with regard to growth parameters, improvement of multisilicon quality. These studies usually involve investigation of crystals at the microlevel [3]. Studies of defects in the crystal structure and the determination of the chemical composition of the material in inclusions can be performed by virtue of scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) that reveal surface effects at the microlevel and determine the chemical composition of the substance.

EXPERIMENTAL

Metallographic studies of the crystal surface structure were first conducted by means of an optical microscope. The objects under study were multisilicon samples grown by the Bridgman method from refined metallurgical silicon and electronic silicon.

For the analysis by SEM and EPMA methods, the surface of multisilicon samples was mechanically ground and polished by diamond pastes, degreased in CCl_4, boiled in distilled water, treated with polishing etchant (a mixture of HF and HNO_3), and subjected to chemical-acid etching (silicon etchant N for a family of {111}, {110}, and {100} planes) according to the ASTM standard.

The crystals were examined on electron probe X-ray microanalyzers in secondary and backscattered electron modes of the electron microscope. For the analysis we used Superprobe-733 and JXA-8200 (JEOL Ltd, Japan) microanalyzers equipped with energy dispersive Sahara (Princeton Gamma-Tech Ltd), EX-84055MU (JEOL Ltd, Japan) and wave spectrometers with crystals LDE1, LDE2, TAP, LDEBH, TAPH, PETJ, PETH, LiF, and LiFH (in five spectrometers on JXA 8200) and TAP, PET, and LiF (in three spectrometers on Superprobe-733). Element distribution maps were obtained by wave spectrometers. The elements in the objects studied were identified using energy dispersive spectrometers.

In order to measure the lifetime of minor charge carriers in multisilicon plates by the contact-free high frequency method, we used a Taumetr 2M device. The bulk lifetime of minor charge carriers was calculated by the international SEMI MF 1535 and MF 28 standards.

RESULTS AND DISCUSSION

The number of intergranular boundaries is different in different parts of multi-silicon crystals. This is well seen in the backscattered electron images of crystal surfaces (Fig. 1). The more homogeneous the crystal surface area is, the better the electrophysical properties can be expected [2]. In the studied multisilicon crystals,

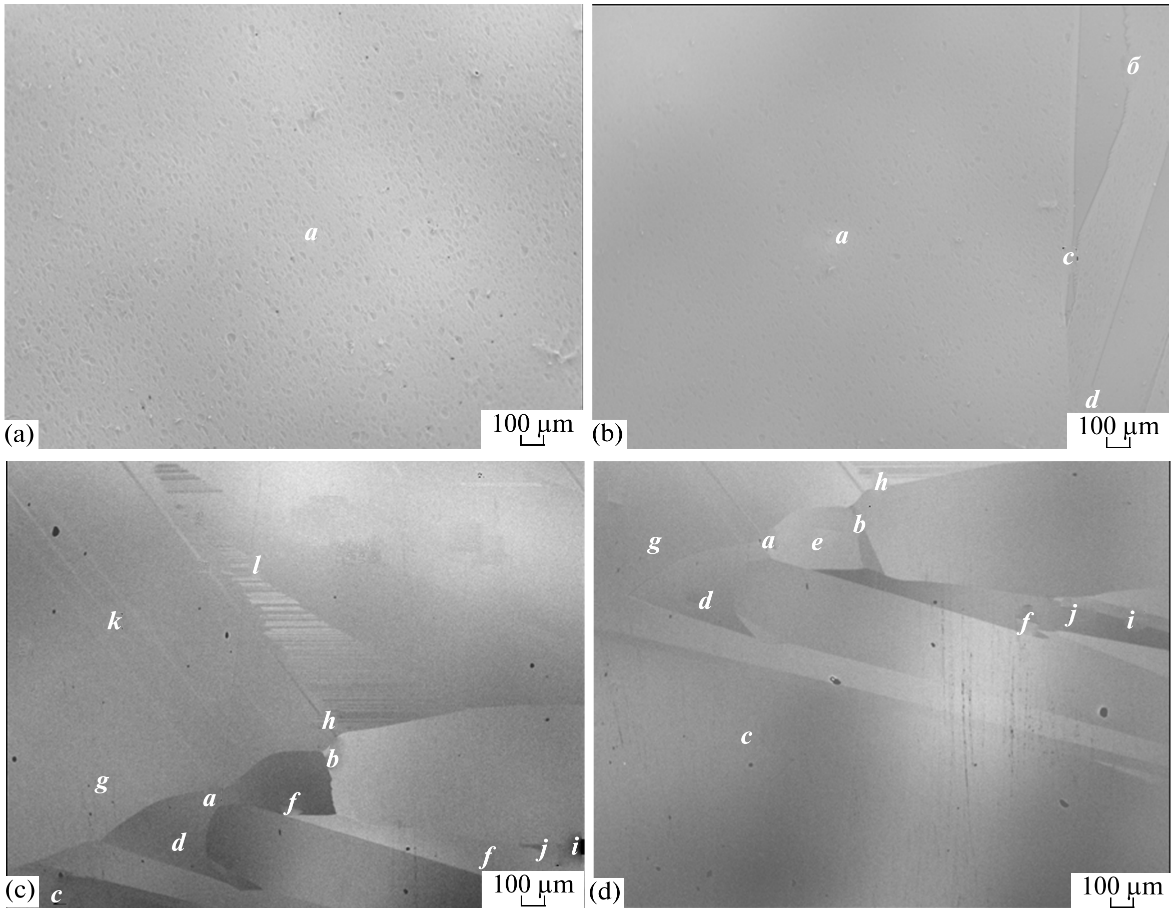

Fig. 1. General view of the polished surface of multi-silicon crystals (backscattered electron image): (a) the defect-free region (*a*), the total size is above 10 mm; (b) the defect-free region (*a*) with a size up to 10 mm and the intergranular boundaries (*b*–*d*); (c, d) two images of the same crystal region (*a*–*h*) obtained when the sample was shifted by 480 μm under the probe.

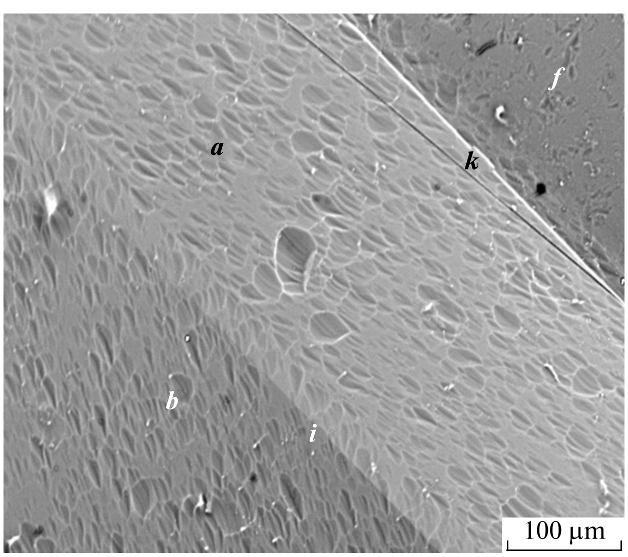

Fig. 2. Etched multisilicon crystal surface (backscattered electron image); *i, k*, and *f* regions correspond to the *f, i*, and *k* regions of the polished surface in Fig. 1d.

separate entire grains without internal intergranular boundaries reach 10 mm or more (Fig. 1a (*a*), Fig. 1b (*a*), Fig. 1d (*c*)). At the same time, some crystal regions consist of fine grains and are characterized by the occurrence of multiple intergranular boundaries (Fig. 1b (*b*, *c*, *d*), Fig. 1c (*a*, *b*, *d*, *e*, *f*), Fig. 1d (*a*, *b*, *f*, *i*, *j*)).

In the backscattered electron imaging mode of the electron microscope, when the sample was moved relative to the electron beam, a change in the image brightness of the same zone was noticed on the surface image. The same regions denoted by the letters *a, b, c, d, e, f, g, h* in Figs. 1c and 1d have different brightness, which is due to the crystallographic orientation of some multisilicon grains. The etching of the surface makes it possible to see the geometry of etching pits of separate blocks, which reflects the crystallographic orientation of grains. The electron scattering effects are different on differently oriented crystals and, consequently, the detector of backscattered electrons, which does not change its position in the microscope, measures a different number of them, and this affects the image brightness of the corresponding crystal regions. The region of the etched multisilicon surface in Fig. 2 corresponds to the regions denoted as *f, j, i* in

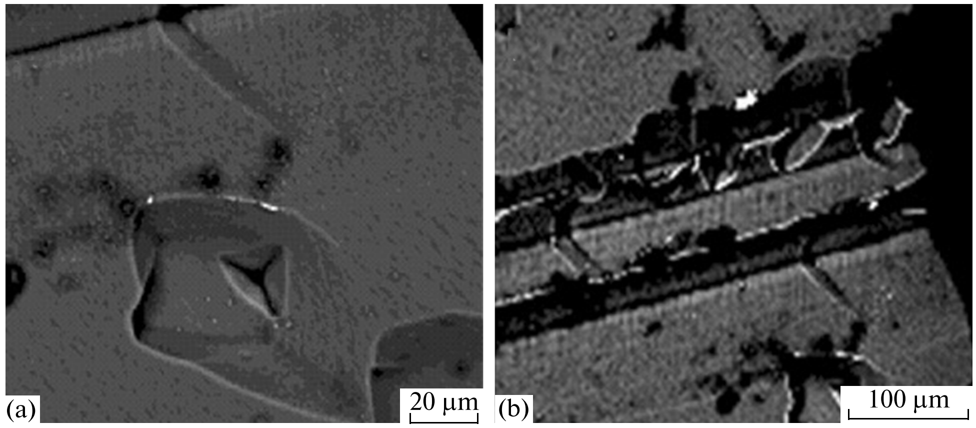

Fig. 3. Iron inclusions found in multisilicon crystals: (a) in a dislocation; (b) at the intergranular boundary decorated by dislocations. Backscattered electron image.

Fig. 1d. It is well seen that the image brightness of the nonetched surface depends on the orientation of the etching pits of the respective region of the etched sample. Thus, by means of the backscattered electron image, it is possible to make a judgment about the different crystallographic orientation of separate multisilicon grains.

From the data of a few different methods determining the impurities in multisilicon [4], the following elements were found to be contained in the studied crystals (in ppm): B 9.5, P 2.5, Mg 1.0, Al 1.3, Ca 4, Ti 0.1, V 0.01, Cr 0.02, Mn 0.01, Fe 1.2, Co 0.01, Cu 0.1, Zn 0.2, Ge 0.12, Sr 0.05, Zr 0.01, Ni 0.1, and Pb 0.03. It is impossible to determine these concentrations by EPMA because the detection limit for the mentioned elements is above 0.00*n*–0.1 wt % and, when they are uniformly distributed in the material, their concentration turns out to be lower than the detection limits of the method. However, almost all these elements were found to be present in multisilicon crystals as inclusions of different shapes and micron sizes. Thus, the inclusion-contained nickel was 3×12 μm; that with vanadium was 1×2 μm, with zinc 2×3 μm; with copper 1.5×2 μm, with bismuth 1×1.2 μm, and with tungsten 3×7 μm; inclusions with titanium reached 1×2 μm, with potassium 2×2.2 μm, with iron 3×16 μm, with calcium 2×2.4 μm, with aluminum 8×10 μm, and with chromium 3×16 μm. The detection of just these elements does not exclude the occurrence (also in the form of small inclusions) of other elements that did not fall into the area of analysis. The randomness and unpredictability of the distribution of the detected element inclusions are responsible for their absence in portions for the analysis by other methods. Inclusions, as a rule, are randomly located in the multisilicon crystal and are detected only when they are thoroughly searched for at high magnification (400- to 600-fold) both outside the boundaries and dislocations and (extremely rarely) in dislocations (Fig. 3a) and at intergranular boundaries decorated by dislocations (Fig. 3b).

In the studied multisilicon crystal, intergranular boundaries of different types occur (Fig. 4), sometimes sawlike (Fig. 4a) or as a jagged line (Fig. 4b), but most of the boundaries represent straight lines (Figs. 4c–f) intersecting at different angles (Fig. 4e, 4f) and parallel to each other (Fig. 1d, boundaries *k*, *i*). The width of intergranular boundaries varies from 0.01–0.1 (Fig. 5b, 4d) to 10 (Fig. 4f) and even to 15–20 μm (Fig. 4c). In the studied crystals, intergranular boundaries are free from impurities, which is observed at both low (Fig. 5a) and high (Figs. 5b, 5c) magnification.

The occurrence of impurities and numerous small grains with different crystallographic orientations in the multisilicon crystal degrades its electrophysical properties—in particular, reducing the lifetime of minor charge carriers (MCCs). In order to establish the dependences between the MCC lifetime and the structural features of multisilicon, the MCC lifetime was measured along and across the crystal growth direction and we investigated the regions in which these measurements were conducted by means of an electron microscope. The main factor responsible for the degradation of the MCC lifetime in multi-silicon turned out to be structural imperfectness—namely, numerous boundaries between different type grains (Fig. 6). Regions a and b in Fig. 6 correspond to the points with coordinates (1.0, 4.5) and (7.0, 4.0) in Fig. 7, in which the MCC lifetime is maximum. The points with coordinates (0.0, 2.8), (2.0, 2.3), and (5.0, 2.2) in Fig. 7 correspond to the minimum values of the MCC lifetime measured in regions c, d, and e (Fig. 6). The dependence is given for the variation of the MCC lifetime along the crystal growth direction. Similar dependences were also obtained in the cross section. It is seen that more homogeneous crystal regions without intergranular boundaries correspond to the maximum values of the MCC lifetime; on the

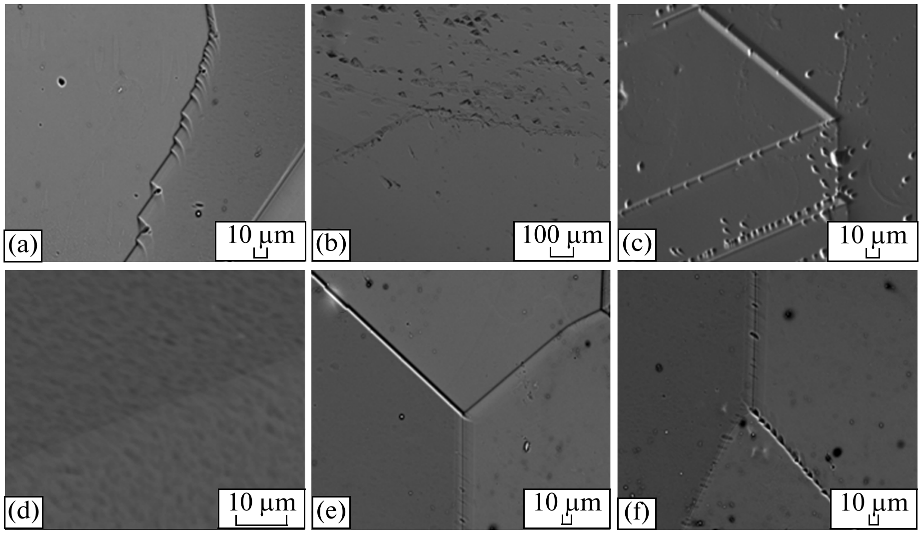

Fig. 4. Intergranular boundaries in multisilicon crystals: (a) sawlike shape; (b) jagged line; (c and d) straight lines; (e and f) straight lines intersecting at different angles. Backscattered electron image.

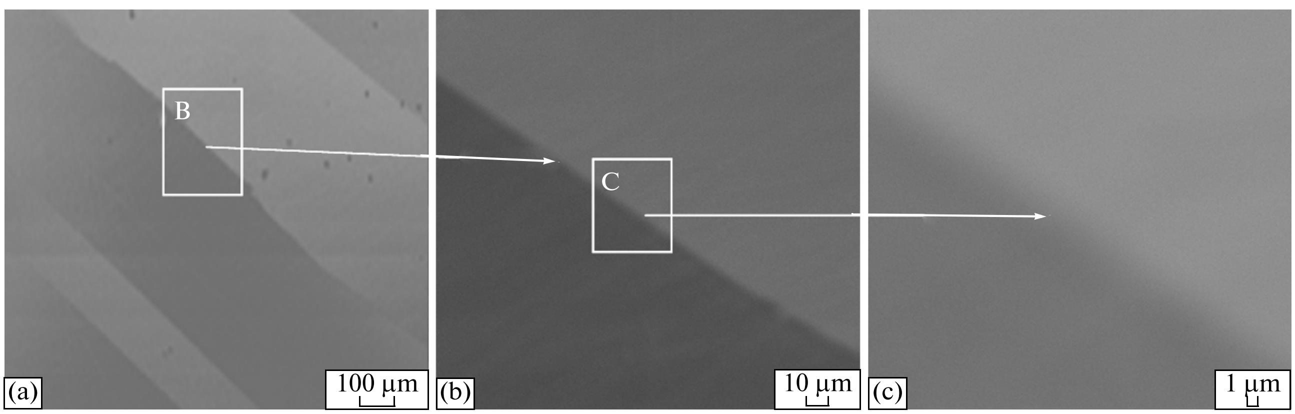

Fig. 5. Intergranular boundaries in multisilicon crystals do not contain impurities: (a) surface area at a level of millimeters; (b) at a level of tens of microns; (c) at a level of 1 μm. Backscattered electron image.

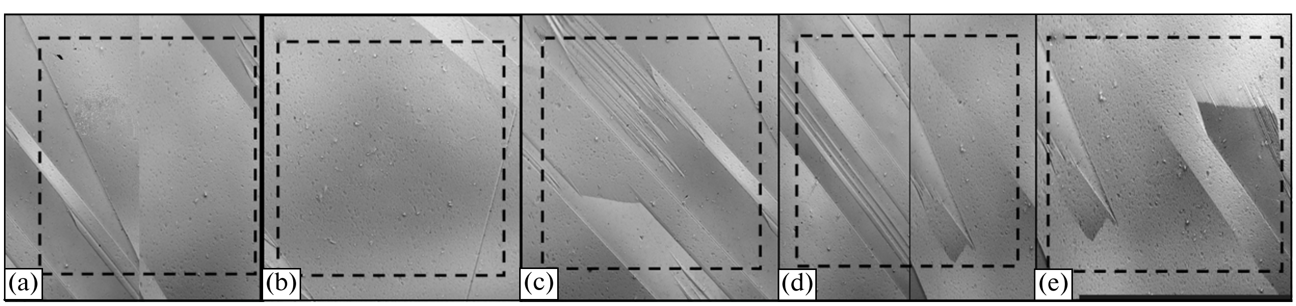

Fig. 6. Regions of chemically polished multisilicon crystal surface in which the MCC lifetime is measured along the crystal growth direction. The area of the marked region in the image is comparable with the Taumetr 2M probe area and is 2×2 mm^2. Backscattered electron image.

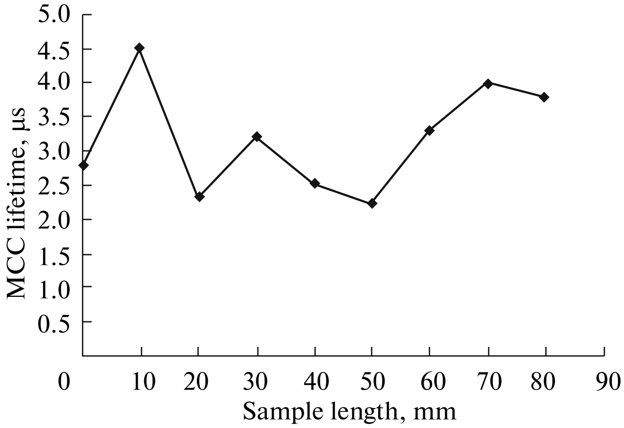

Fig. 7. Variation of the MCC lifetime measured along the crystal growth direction. Points in the plot correspond to the regions in which the MCC lifetime was measured: the point with coordinates (1.00, 4.50) corresponds to the measurement in the region marked in Fig. 7a, (7.00, 4.00) corresponds to 7b, (0.00, 2.80) to 7c, (2.00, 2.30) to 7d, and (5.00, 2.20) to 7e. The MCC lifetimes were measured by R.V. Presnyakov on a Taumetr 2M device.

contrary the minimum values are related to the crystal regions that contained numerous intergranular boundaries. We failed to find the effect of inclusions because of their absence in those regions where the lifetime was measured. This once again confirms the heterogeneous unpredictable distribution of inclusions over the crystal and their absence at the intergranular boundaries.

CONCLUSIONS

Thus, the study of multisilicon crystals by electron microscopy and electron probe microanalysis made it possible to reveal the types of intergranular boundaries. It is found that impurity elements are contained in inclusions with a high probability. Intergranular boundaries and dislocations contain almost no impurities, and the elements present in multisilicon are not concentrated on them. It is established experimentally that the maximum lifetime of minor charge carriers corresponds to the homogeneous regions of the multisilicon crystals, whereas the minimum value corresponds to the regions with numerous intergranular boundaries in both the axial and cross sections of the crystal.

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