X-RAY PHASE ANALYSIS OF IMPURITIES IN SILICON CRYSTALS MADE FROM METALLURGICAL SILICON WITH DIRECTIONAL CRYSTALLIZATION

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The control of impurities at each stage of the purification process of Si is the primary topical problem in Si technology. The technique of determining the impurity composition should be multi-element and with low limit-detection of impurities. From this point of view, X-ray analysis of the phase composition of Si, based on the identification of X-ray diffraction lines is very attractive. Obtaining of Si directly from MG-Si is essential to reveal the physical possibilities of the directional crystallization. In this work, there are considered the options on a set of detectable impurities and the limits of their detection in such type of Si by X-ray diffraction method. It has been shown, that applicability of X-ray analysis of the phase composition of Si, based on the identification of X-ray diffraction lines, depends on the stage of Si purification.

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Introduction

Silicon is the main component of the modern efficient semiconductor devices including micro-, opto-, nanoelectronics. Silicon has many advantageous properties like the high photo and low temperature sensitivity, minimal reflection losses, therefore the 85 % of solar batteries are made from silicon. Nowadays and in the nearest future, silicon is an irreplaceable material and holds leading position among the semiconductor materials and optoelectronics.

The silicon mainly used in its crystalline or amorphous/crystalline thin film (epitaxial layers) forms on various substrates. The impurity composition of silicon request depends on the using field of silicon. Depending on the primary purpose of Si application there are three distinct Si product form: electronic quality Si, “solar” Si and metallurgical (technical) Si. Type of silicon must be supplied with exceptionally specified impurities to provide the defined expected parameters of Si.

Following and determination of these impurities are an essential step of the silicon production technology. Comparing the methods of silicon purity analysis, the number of simultaneously detectable impurities, the limit of their detection, the availability of the necessary equipment, the duration of the investigation and its cost have to take into consideration.[1-5]

We have developed a method which can be used for analysis of all kind of silicon products including metallurgical, "solar", integrated circuits and other silicons, etc., and in the most cases, which is multi-element and has low limit-detection of impurities. This method is based on [the] X-ray phase analysis of Si, based on the identification of X-ray diffraction lines. The goal of the present article is the investigation of the possibility to determine the composition of detrimental impurities in Si crystals, obtained by pulling directly from metallurgical grade Si (MG-Si) melt.

Experimental

In the experiments, metallurgical Si (*n*-MG-Si) with ~98.3 wt.% Si content and detrimental impurities of Fe, Al, P, Ca, Cu, Mg, Mn, Ni, and Ti was used. The Czochralski growth method of pulling crystals has been used for obtaining Si directly from MG-Si melt. Crystals have been grown from quartz crucible as described in our previous work.[6]

Microstructure has been examined under Neophont optical microscope. The specimens were chemically polished in a mixture of HNO_3 + HF (1:1) acids, washed with distilled water, and etched for 1–5 min in an alkaline solution of 30 % KOH at 50–100 °C.

Electrical properties (Hall effect and conductivity) measurements have been implemented by a standard dc bridge technique.

The content of contaminating impurities in *n*-MG-Si before and after the directional crystallization has been defined by X-ray diffraction method, micro X-ray spectral and emissive spectral analyses. X-ray investigations have been implemented on modernized X-ray diffractometer DRON–4–07 with software applying molybdenum radiation at the continuous regime of filming by 0.5 degrees min^{-1}.

Results and discussion

Initial experimental material of metallurgical silicon with 98.30 wt.% Si and undesirable impurities up to ~2 wt.% is the first step product of Si obtained by restoration from quartzite with reaction to carbon. MG-Si was a multiphase substance with n=1.2·10^{18} cm^{-3}. The appropriate microstructure and X-ray diffractogram of MG-Si are shown in Figs. 1 and 2, respectively.

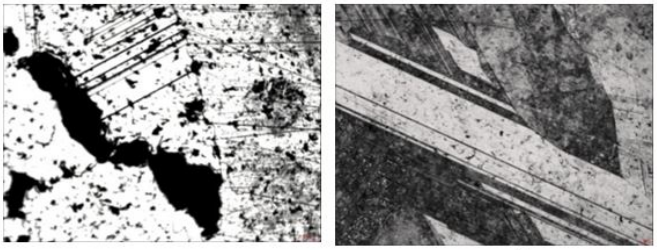

Figure 1. Microstructure (×100) of Si experimental samples of different purity. (a) *n*-MG-Si and (b) pulled with a rate of 0.3 mm min^{-1}.

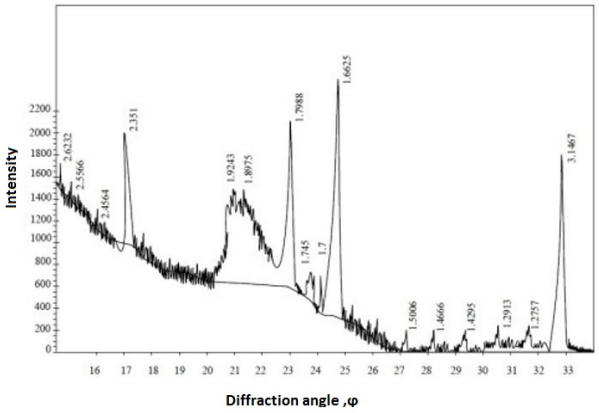

Figure 2. The x-ray diffraction pattern of *n*-MG-Si.

Fig.1a shows traces of inclusions of eutectic phases formed from impurities Mg, Mn, Cu, Fe, Ni, Ti Al, Ca and the silicon in MG-Si. The solubility of impurities in Si is much less in solid phase than in liquid state,[7] and their concentration exceeded the limit of their solubility in the silicon. As a result, impurities could not form solid solutions with silicon and precipitated as inclusions in the silicon matrix. Since phase composition cannot be judged from the chemical analysis data, X-ray structural phase analysis makes it possible to obtain the necessary information. The complex picture of the multiphase state of *n*-MG-Si is reflected in the X-ray diffractogram (Fig. 2).

The x-ray diffraction pattern of an experimental sample of MG-Si shown in Fig. 2 is typical for multiphase MG-Si having a significant number of impurities. Fig. 2 identifies each phase of multicomponent of MG-Si and makes it possible to determine their percentage.

After pulling of the crystal of MG-Si from the melt at ~0.30 mm per minute rate the experimental sample of *n*-MG-Si (n=1.2·10^{18}cm^{-3}) goes into *p*-type Si with 99.99 wt.% Si content, current carriers concentration was found to be 2·10^{16} cm^{-3} and mobility of them was 510 cm^2 V^{-1}·s^{-1}. It means that MG-Si has been purified from the majority of impurities by 1.5–3 orders up to 99.99 wt.% Si with impurity content of ~10^{-2} wt.%.This result could be confirmed by microstructure (Fig. 1b) and X-ray phase analyses (Fig. 3). Fig. 1b shows that after pulling of MG-Si from melt the tracks of inclusions of different phases, observed in the initial microstructure of MG-Si have disappeared and matrix become single-phase with dense structure.

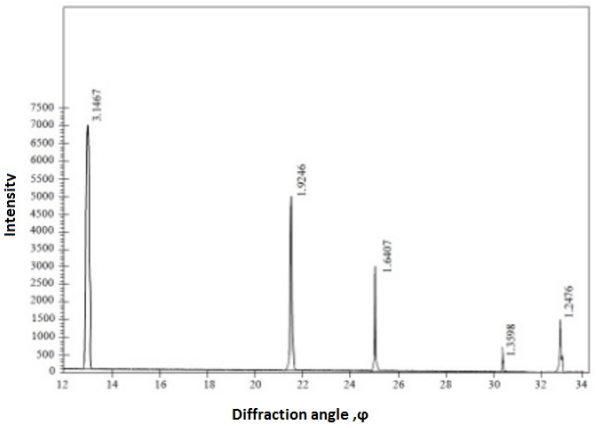

Figure 3. The x-ray diffraction pattern of purified pulled Si from MG-Si melt.

It is known, that a crystalline phase of the substance has the characteristic diffraction pattern that distinguishes it from other substances. Therefore, identification of the X-ray lines in the diffractogram (Fig. 3) has been conducted by the comparison of the diffractogram of experimental Si under study with the diffractogram of known Si standards (Fig. 4).[8] The interplanar distances *d* for all lines for different (*hkl*) has been calculated by the fundamental law of high-resolution X-ray spectroscopy (Wulff–Bragg‘s equation). The data of the interplanar distances and the intensity of the main lines on the X-ray diffractogram of Si pulled from the melt of *n*-MG-Si are placed in Table 1 in descending order.

Table 1. Interplanar distances and main lines intensity (in brackets) on X-ray diffractogram of Si pulled from a melt of *n*-MG-Si.

Si[8]	Si pulled from the melt			
	1	2	3	4
3.138 (100)	3.1467 (100)	3.1467 (100)	3.1486 (100)	3.1486 (100)
1.920 (60)	1.9246 (60)	1.9253 (60)	1.9260 (60)	1.9253 (60)
1.630 (35)	1.6407 (35)	1.6413 (35)	1.6413 (35)	1.6413 (35)
1.357 (8)	1.3598 (8)	1.3605 (8)	1.3609 (8)	1.3609 (8)
1.246 (13)	1.2476 (13)	1.2482 (13)	1.2482 (13)	–

The intensities of all the diffraction lines measured are expressed as a percentage of the strongest line to which the value of 100 % is attributed too. The intensity of diffraction

maxima depends on the chemical composition of the Si crystal.

The coincidence (within the measurement error) of the experimental and tabulated values of Reference Book of the interplanar distances and relative line intensities make it possible to identify the phases present in the material uniquely.

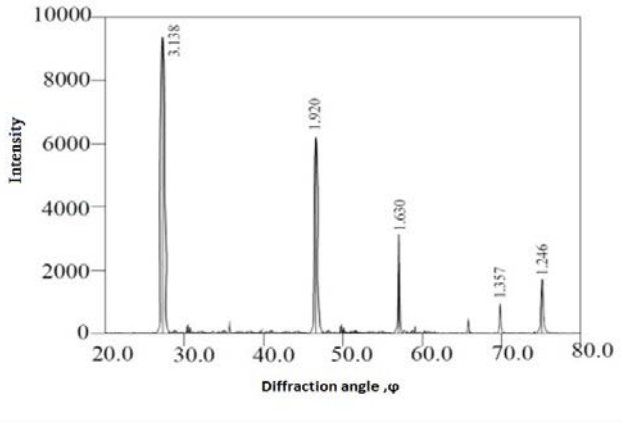

Figure 4. X-ray diffraction patterns of standard pure Si.

All basic diffraction maxima for pure standard Si (Fig. 4) are revealed in the X-ray diffraction pattern of purified Si (Fig.3).[8]

As can be seen from Fig. 3 and Fig. 4, pulled Si is single-phase, and the residual impurities in quantity of 10^{-2} wt.% cannot be fixed by X-ray diffraction analysis. Residual impurities are reflected in electrical properties (n=1.2·10^{16} cm^{-3}) and are detected by emission spectral analysis. This indicates, that the X-ray diffraction analysis of silicon purity is limited by 99.99 wt.% Si and does not have sufficient sensitivity to detect impurities in an amount of $<10^{-2}$ wt.%, thus X-ray diffraction method is suitable for analyses of Si purity only up to 99.99 wt.% Si level. For increasing the sensitivity of X-ray analysis, it is necessary to combine it with other methods.

Conclusion

In this paper, we considered the possibilities on a set of detectable impurities and the limits of their detection by X-ray diffraction method. The presented way is a multi-element analysis and one of the effective methods for simultaneous determination of the impurity composition of silicon. The limits of detection of the amount of detectable impurities are shown.

The application of X-ray diffraction method to Si depends on the stage of its purification. The content of contaminating impurities before and after purification has been established by X-ray spectral microanalyzer and emissive spectral analysis too.

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