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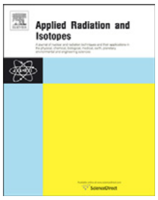

Fast determination of impurities in metallurgical grade silicon for photovoltaics by instrumental neutron activation analysis

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ABSTRACT

Standard wafer solar cells are made of near-semiconductor quality silicon. This high quality material makes up a significant part of the total costs of a solar module. Therefore, new concepts with less expensive so called solar grade silicon directly based on physiochemically upgraded metallurgical grade silicon are investigated. Metallurgical grade silicon contains large amounts of impurities, mainly transition metals like Fe, Cr, Mn, and Co, which degrade the minority carrier lifetime and thus the solar cell efficiency. A major reduction of the transition metal content occurs during the unidirectional crystallization due to the low segregation coefficient between the solid and liquid phase. A further reduction of the impurity level has to be done by gettering procedures applied to the silicon wafers. The efficiency of such cleaning procedures of metallurgical grade silicon is studied by instrumental neutron activation analysis (INAA). Small sized silicon wafers of approximately 200 mg with and without gettering step were analyzed. To accelerate the detection of transition metals in a crystallized silicon ingot, experiments of scanning whole vertical silicon columns with a diameter of approximately 1 cm by gamma spectroscopy were carried out. It was demonstrated that impurity profiles can be obtained in a comparably short time. Relatively constant transition metal ratios were found throughout an entire silicon ingot. This led to the conclusion that the determination of several metal profiles might be possible by the detection of only one "leading element". As the determination of Mn in silicon can be done quite fast compared to elements like Fe, Cr, and Co, it could be used as a rough marker for the overall metal concentration level. Thus, a fast way to determine impurities in photovoltaic silicon material is demonstrated.

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1. Introduction

In standard silicon solar modules, the costs of silicon wafers make up 50% of the total costs (Götzberger et al., 2002). One reason is the high costs for near-semiconductor quality feedstock with purities of 99.99999% (7 N) to 99.999999% (8 N), as purification steps are time and resource consuming. Low-cost silicon, such as metallurgical grade (MG) and upgraded metallurgical grade (UMG) silicon with purities of approximately 2–3 N and 3–5 N could be used for new solar cell concepts, although there are various issues one has to face regarding this material. One of the crucial problems is the high amount of metallic impurities, for example Fe or Cr. These contaminations degrade the minority carrier lifetime and therefore the solar cell efficiency by forming recombination centers. Istratov et al. (2006) demonstrated that the distribution of metals in multicrystalline silicon has a crucial impact on the lifetime. The cell efficiency is less affected by metals in precipitates than by interstitial impurities even at lower densities. Nevertheless, starting with MG silicon, it is still important to reduce the overall concentration of transition metal impurities. Directional solidification and gettering are two ways of silicon purification.

Crystallization of silicon feedstock is an early step in the solar cell process whereby the amount of metallic impurities is reduced by several orders of magnitude. The silicon feedstock is melted in a crucible and crystallized to an ingot by unidirectional solidification, which occurs from the bottom upwards. Thereby, the metallic impurities are accumulated at the top of the ingot due to the very small segregation coefficients of metals in silicon. For example, Fe and Cr have segregation coefficients of 7×10^{-6} and 3×10^{-6}, respectively (Weber, 1983). The resulting silicon ingot is cut into wafers, which contain very different amounts of metals depending on the horizontal position in the former ingot.

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In addition, gettering steps are considered to be essential in the cell process to further reduce the metal content. In this work, a new gettering technique with hydrogen chloride (HCl) gas was applied. The gettering effect is due to the removal of metals from the surface of the wafers through the formation of volatile chloride compounds (Istratov et al., 2000). These compounds are transported away by the stream of gas, and further diffusion of the metals from the bulk to the wafer surface occurs. The diffusion depends on the diffusion coefficient of the respective metals. For example, Fe has a diffusion coefficient of 4×10^{-6} cm^2/s at 1100 °C (Weber, 1983).

Both above-mentioned procedures of silicon purification need to be evaluated by analytical techniques to learn about their effectiveness. A suitable analysis method is needed for the detection of metallic impurities in solar grade silicon. The ideal analysis technique should be able to detect detrimental transition metals, such as Fe and Cr, over a wide concentration range in solar grade silicon with very low detection limits. The technique should be a fast procedure without extensive sample preparation, ideally without the need to dissolve the silicon. This reduces the risk of contamination during sample preparation.

Instrumental Neutron Activation Analysis (INAA) is well known and established in many different research and application areas. A lot of experience has been made applying INAA to transition metal impurities in silicon, especially in crystalline silicon (see e.g. Wiehl et al. (1982), Verheijke et al. (1989) and Istratov et al. (2003)). However, the determination of transition metals, such as Fe, Cr, and Co in silicon, which is performed using long-lived nuclides, takes a relatively long time. In this work, INAA was investigated as a possible analytical technique to control the above-mentioned procedures of silicon purification with the goal of a high sample throughput. Due to the segregation coefficients, the ratios of various transition metals along the crystallization front should be constant. Therefore, it was tested if the concentration profile of the transition metals could be determined by measuring only the profile of Mn as the "leading element". Mn has a high activation cross-section of 13.3 b and a half-life of 2.58 h. Consequently, quick scans of the impurity profile along the crystallization front should be possible. Therefore, we investigated the analysis of silicon columns cut from an ingot along the crystallization front.

2. Experiments

2.1. Sample preparation and analysis of Si wafers

After unidirectional crystallization of MG-Si feedstock with 99.3% purity, the ingot was cut into wafers. From three different parts of the ingot (top, middle, and bottom), wafers were cut into samples with a size of approximately $2.5\times1.25\times0.027$ cm^3 and a weight of approximately 200 mg. Afterwards, the samples were surface cleaned by chemical polishing (etching of the silicon surface by a mixture of hydrofluoric acid, acetic acid, and nitric acid) and irradiated at the research reactor TRIGA Mark II in Mainz (Hampel et al., 2006) and at the research reactor FRM-II in Garching, respectively. After irradiation and decay of the background, which is caused by the beta emitter ^{31}Si, the samples were measured with a high purity germanium (HPGe) semiconductor detector with a relative efficiency of 27.7% at the Institute of Nuclear Chemistry at the University of Mainz. Similar INAA measurements were also carried out with wafers, which were treated by HCl gas gettering and analyzed together with untreated neighboring wafers as reference to evaluate the efficiency of this new gettering technique.

The determination of Ni was achieved by the ^{58}Ni(n,p)^{58}Co reaction. All other elements were determined by (n,γ) reactions. For all analyses, high purity liquid standards of the elements Cr, Mn, Fe, Co, and Ni were irradiated and measured together with the samples. For data evaluation, the software Genie 2000 V2.1 (Canberra) was used. The applied irradiation protocols are listed in Table 1.

2.2. Sample preparation and analysis of Si columns

Vertical columns with a size of approximately $1\times1\times20$ cm^3 were cut out of an ingot, which was crystallized out of upgraded metallurgical grade silicon feedstock. These columns were irradiated as a whole in the central irradiation position at TRIGA Mainz for 6 h at a neutron flux of 4×10^{12} cm^{-2} s^{-1}. Standards of Mn and As were placed at the top and bottom of the column for the determination of the absolute metal content. After a decay time of 15 h, the columns were measured with a germanium detector with a relative efficiency of 67% whereby a collimator of lead with 10 cm thickness and a slit width of 1 cm was placed in front of the germanium detector (Fig. 1). For the measurements the columns were divided in two pieces of 10 cm length. The influence of non-perfect shielding of the collimator, i.e. gamma rays penetrating the lead, can be estimated from the mass attenuation factors of lead for the relevant energies. The estimations show that within all other uncertainties of the measurements the collimator can be assumed to be nearly perfect.

The columns were scanned in 1 cm steps. The ^{31}Si activity was used to control and correct deviations of the neutron flux along the column. The overall uncertainties were calculated from all contributing errors, which are listed in the following in the order

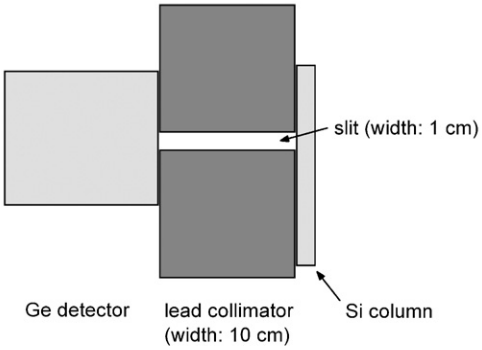

Fig. 1. Schematic (top view) of collimator for scanning Si columns (not to scale).

Table 1
Irradiation protocols used for analyses of the wafers after crystallization.

Program no.	Irradiation facility	Irradiation time (h)	Decay time	Measuring time (h)	Neutron flux (cm^{-2} s^{-1})	Investigated elements
1	TRIGA Mainz	33	approx. 8 d	15	4.2×10^{12}	Ni
2	TRIGA Mainz	3	approx. 3 h	0.5	4.2×10^{12}	Mn
3	FRM-II Garching	90	approx. 21 d	15	1.1×10^{14}	Cr, Fe, Co

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