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Purification of melt-spun metallurgical grade silicon micro-flakes through a multi-step segregation procedure

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ABSTRACT

Melt-spun metallurgical grade (MG) micron dimension silicon flakes have been purified into near solar grade (SG) quality through a multi-step melting and re-solidification procedure. A wet oxidation-applied thermal oxide maintained the sample morphology during annealing while the interiors were melted and re-solidified. The small thickness of the flakes allowed for near elimination of in-plane grain boundaries, with segregation enhanced accumulation of impurities at the object surface and in the few remaining grain boundaries. A subsequent etch in 48% hydrofluoric acid (HF) removed the impure oxide layer, and part of the contamination at the oxide–silicon interface, as shown by electron dispersive spectroscopy (EDS) and backscattered electron imaging (BEI). The sample grains were investigated by electron back-scattered diffraction (EBSD) after varying numbers of oxidation-annealing-etch cycles, and were observed to grow from $\sim$5 μm to $\sim$200 μm. The concentration of iron, titanium, copper and aluminium were shown by secondary ion mass spectroscopy (SIMS) and inductively coupled plasma mass spectroscopy (ICPMS) to drop between five and six orders of magnitude. The concentration of boron was observed to drop approximately one order of magnitude. A good correlation was observed between impurity removal rates and segregation models, indicating that the purification effect is mainly caused by segregation. Deviations from these models could be explained by the formation of oxides and hydroxides later removed through etching.

1. Introduction

Today's photovoltaic (PV) production is strongly dominated by wafer-based modules made from either single- or multi-crystalline silicon. Due to both the requirement for purity, and the significant material waste during the production of wafers, the price for these PV cells is high, motivating research on alternative materials and designs. One class of alternative designs relies on micro- or sub-micro-scale geometries that increase the junction area of the cell per unit of silicon, for example sliver, spherical and vertical rod radial cell designs [1–4]. These designs exploit different cell morphologies to lower the amount of silicon used, enhance absorption, and reduce the requirement for long carrier diffusion lengths [5].

Common problems with the above mentioned designs are polycrystallinity as well as the high level of impurities within the material. For example in the silicon micro-sphere design, high supercooling during formation causes the spheres to be polycrystalline and to have a high density of defects [6,7], increasing the effective solubility of impurities. Various methods have been used to remove these defects and increase the crystallinity, ranging from the use of catalyst agents [6] to various melting and re-solidification approaches [4,8–11]. The latter approach has proven most successful, as the listed studies all managed to produce near perfect micro-sized single crystalline spheres from multi crystalline as-dropped starting material.

Motivated by the fact that sub-mm spherical Si particles can be successfully melted and recrystallized into near single crystals, we present here results of a general segregation-based iterative purification process. This procedure is performed on rapidly produced metallurgical grade silicon samples with dimensions of tens of microns and flake-like morphology. Segregation, together with the absence of in-plane grain boundaries, results in enhanced accumulation of impurities on the sample surface, where they are accessible for the removal through wet chemical methods. For net-shape applications, this may eliminate the demand for a high purity starting material, as the silicon can be purified while in its intended final form. The process is applicable to micro-sized objects of any shape.

The suggested process is similar to acid leaching, but without the need for costly grinding [12,13]. As the samples are produced and kept in their intended final form throughout the treatment,

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the process can be repeated multiple times in order to increase the purity. The leaching agent is chosen to be HF following Juneja et al. [14] where they demonstrated the feasibility of turning MG silicon into SG. A similar method was tried out earlier by Gharghi et al. [11] who measured the segregation of boron, phosphorus and aluminium in spherical silicon micro spheres made through a dropping process from high purity starting material. They concluded that their solidification velocity was too high to achieve segregation and that the effective segregation coefficient [15,16] thus approached unity. However, Refs. [17–20] observed segregation with much higher cooling rates; different nucleation conditions and impurity concentrations are possibly responsible for the divergent data. In order to re-evaluate the approach of Gharghi et al. we present here a proof of principle study where we have assessed the removal of a selection of impurities with varying segregation coefficients.

2. Experimental

The samples were made through a melt-spinning process where MG-silicon was melted through rapid induction heating in a graphite crucible, and sprayed down on a rotating copper wheel using argon over-pressure. This is similar to the approach of Forwald et al. [21], and a schematic illustration of the experimental set up can be seen in Fig. 1. To reduce oxidation of the samples, the process was conducted in a chamber purged with argon several times before the melt-spinning was performed under a continuous flow of argon at 0.8 bar. The distance between the crucible and the wheel was set to ≈ 0.5 cm and the crucible nozzle was sharpened at the tip in order to reduce adhesion of the exiting melt. The resulting samples had mixed morphologies, with the majority being flakes extending $\approx 0.3 \times 0.3$ cm with thicknesses typically ~ 30 μm (Fig. 2). The copper wheel was polished prior to use so as to remove any irregularities on the wheel surface causing inconsistent results. This may have caused some copper to be introduced into the samples due to transfer of loose copper particles from the copper wheel surface.

2.1. Purification procedure

The flakes are made of MG-silicon ($\approx 98\%$ Si) and need to be purified before they can be used in the production of solar cells [22].

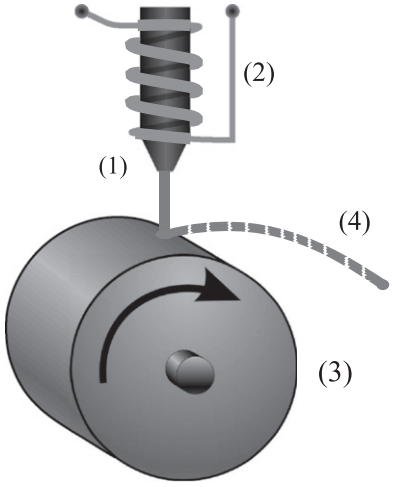

Fig. 1. A schematic illustration of the experimental setup used to produce silicon micro-flakes. Metallurgical grade silicon is melted in a graphite crucible (1) using induction heating (2) and sprayed down onto a rotating copper wheel (3). When hitting the rotating wheel, the silicon solidifies rapidly into small flakes (4).

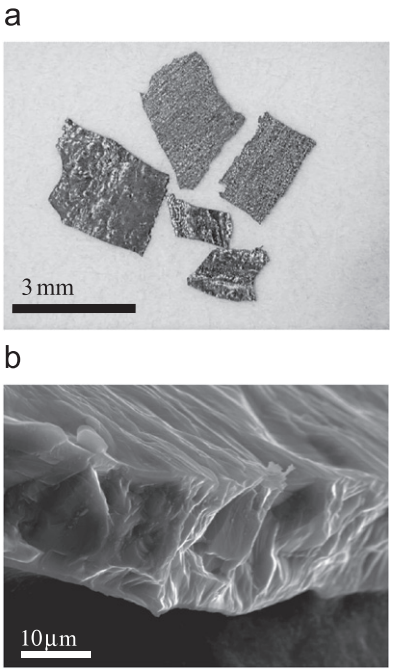

Fig. 2. A conventional optical micrograph of the flakes as-made by melt spinning (a) and a scanning electron micrograph of a cross-section (b). The flakes are typically 1–3 mm in the *xy*-plane with a thickness measuring several tens of microns.

A purification process, motivated by the segregation properties of various impurities between liquid and solid silicon, is chosen for turning the MG silicon into SG. As all transition metals have, in silicon, equilibrium segregation coefficients markedly differing from unity [22], a coarsening of the grain structure through melting and controlled re-solidification will force impurities to the surface, making them easy to remove by chemical methods. A cyclic process was thus performed consisting of melting, re-solidification and etching in order to obtain a satisfactory level of purity (this process will be referred to as a purification cycle). Thermal oxidation was performed between cycles to stabilize the flake geometry.

The samples were initially given a $\approx$ 2 min etch in 48% HF in order to remove impurities and/or oxide formed on the surface during melt-spinning. Such impurities would prevent the formation of a defect free thermal oxide layer, which would increase the probability of sample deformation during subsequent annealing. Also, impurities present in the starting material have accumulated on the surface of the flakes (Fig. 3a). The initial etch will thus not only remove impurities introduced during fabrication, but also these surface impurities. This can be seen in Fig. 3, where most surface impurities evident on grain boundaries are removed during the initial HF etch-step.

A thermal oxide was grown on the samples prior to annealing, preventing deformation and reducing adhesion to the quartz crucible when the silicon flake was melted [23]. Other temperature resistant coatings such as silicon nitride could also be used. However, according to Appapillai et al. [23], thermally grown silicon oxide is ideal for maintaining the morphology during melting of the silicon interior.

The wet thermal oxide was grown at 1150 °C for 3 h using a conventional tube furnace, and the thickness of the oxide layer was measured with a Jeol JSM 840 SEM to be $\approx$ 700 nm. During the subsequent annealing, the samples were heated to ≈ 1440 °C in a normal air environment and held there for 1–2 min in order for the silicon interior to fully melt. This temperature is above the melting