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Densification and microstructure evolution during sintering of silicon under controlled water vapor pressure

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Abstract

Sintering of fine silicon powder was studied under controlled water vapor pressures using the Temperature–Pressure–Sintering Diagram approach. The water vapor pressure surrounding the sample was deduced from thermogravimetric analysis and related to the water content of the incoming gas flux with a simple mass transfer model. The thickness of the silica layer covering silicon particles was then monitored by the water vapor pressure and the microstructure evolution and densification during sintering could be controlled. Stabilizing the silica layer indeed inhibits grain coarsening and allows better densification of the compacts under humidified atmosphere as compared to dry atmosphere.
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Keywords: Silicon; Sintering; Atmosphere control; Microstructure evolution; Kinetics

1. Introduction

Silicon is largely available on earth, but photovoltaic applications require crystallization of silicon ingots of high purity obtained through high energy consuming processes. Ingot cutting is responsible for a large material loss and leads to expensive production costs. Sintering of near net shape silicon wafers is thus an important issue.

Previous works showed that densification of silicon is not favored during sintering because of significant grain coarsening. Depending on the authors, the coarsening mechanism could be surface transport [1,2] or vapor transport [3–5]. Actually, both mechanisms can dominate sintering kinetics, depending on the stability of the silica layer at the silicon particle surface [6–8].

Recently, Temperature–Pressure–Sintering diagram approach (TPS diagrams) [9] has been proposed to monitor the silica layer reduction kinetics in order to control the sintering kinetics of silicon, *i.e.*, microstructure evolution and densification.

In this paper, oxidation kinetics of silicon powder compacts, *i.e.*, the thickness of the silica layer at the particle surfaces, is monitored by controlling the water vapor pressure surrounding the sample as a function of the temperature cycle using thermogravimetric analysis. A promising gain of 15% is observed on the final density for samples sintered under humidified atmosphere compared to dry atmosphere. Eventually, the importance of the furnace geometry design on sample mass loss is discussed.

2. Experimental procedure

2.1. Powder and powder compact characteristics

The powder consists of fine spherical particles of 220 nm estimated from BET specific surface area measurements ($11.7\,m^2\,g^{-1}$, Micromeritics ASAP 2020). The morphology of the powder is observed using FEG-SEM (CARL ZEISS ULTRA55). The oxygen content (0.61 wt.%) is estimated from an instrumental gas analysis (IGA ELTRA ON900). The thickness of the native oxide layer calculated from the oxygen content

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and the specific surface area is 0.43 ± 0.10 nm. The global amount of metallic impurities is less than 1 ppm.

Cylindrical compacts (54% relative density) are obtained by uniaxial pressing at 50 MPa followed by cold isostatic pressing at 450 MPa. Samples are about 400 mg mass, 7 mm diameter and approximately 8 mm height.

2.2. Thermogravimetric measurements and humidity controller system

Thermogravimetric analyses (TGA) are performed in a SETARAM Setsys apparatus. Compacts are hung up to a tungsten suspension in order to limit interactions with silicon. He-4 mol.% H_2 carrier gas ($2\,l\,h^{-1}$) is used to avoid the oxidation of the tungsten part.

The furnace temperature, T, is monitored with a tungsten-rhenium thermocouple and is homogenous over a range of 30 mm. In this part of the tube, the atmosphere can be assimilated as quasi-stagnant, *i.e.*, the transport of mass species can be considered as essentially diffusive [7].

The water vapor pressure is monitored with a humidity controller system made of two gas lines. One line is the carrier dry gas while the other is obtained by circulating the carrier dry gas in a water container. Both gases are mixed and a humidity probe controller (Vaisala HUMIDICAP® HMT333 – West N8800) allows to regulate thermal mass flow (Brooks SLA5850S) to give a water vapor pressure, $P_{H_2O}^{Probe}$, comprised between 100 and 2000 Pa.

The microstructure of the sintered compact is observed on polish surfaces using FEG-SEM and sample densities are measured using the Archimedes method.

3. Theory

3.1. Temperature–Pressure–Sintering diagram

Silicon sintering kinetics is strongly affected by the presence of a silica layer at the silicon particle surface. This behavior is described in Fig. 1 using a Temperature–Pressure–Sintering diagram approach [9].

Using thermogravimetric experiments the reduction kinetics of the silica layer under standard He-4 mol.% H_2 ($2\,l\,h^{-1}$) atmosphere has been studied for powders of various particle size [6]. The silica layer does not preclude the $SiO_{(g)}$ release at temperatures above 1000 °C, so that the reaction (R_1) controls the stability of the silica layer.

$$Si_{(s)} + SiO_{2(s)} = 2SiO_{(g)} \quad (R1)$$

The conditions for the stability of the silica layer can then be given in terms of silicon monoxide partial pressure, P_{SiO}, as a function of the temperature, as represented at the top of the TPS diagram in Fig. 1. The effect of the silica layer on silicon sintering kinetics can be estimated using appropriate approximations [9]. This can be summarized using a sintering diagram approach [11], where x is the neck size radius between two connecting spherical particles of radius a.

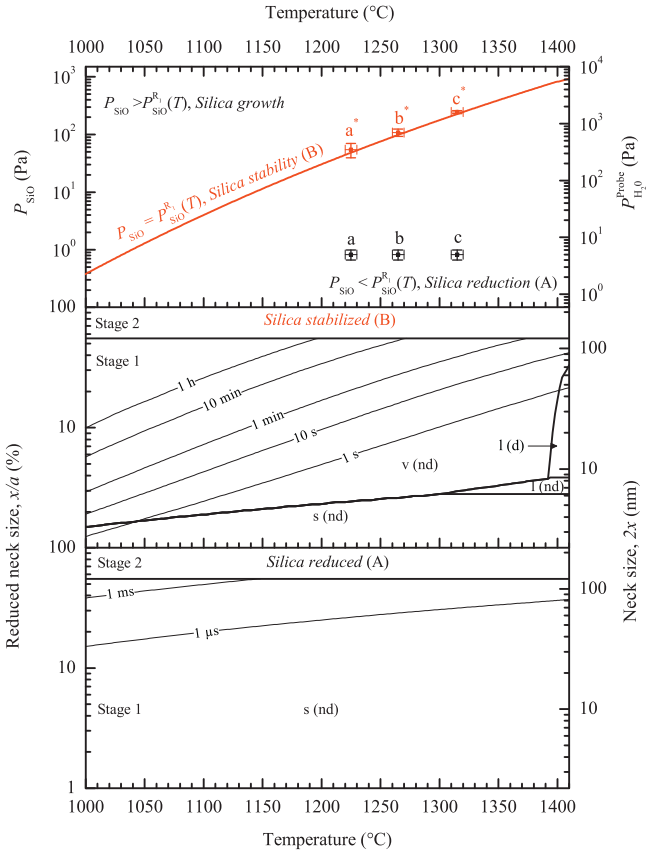

Fig. 1. Temperature–(water vapor) Pressure–Sintering rate (TPS) diagram. Lines of constant sintering time are calculated for particles with a diameter $2a = 220$ nm. Top of the diagram: silicon monoxide pressure, P_{SiO}, or probe water vapor pressure, $P_{H_2O}^{Probe}$, at which the silica layer ought to be stabilized with respect to the temperature. Section (A): Neck growth kinetics with reduced silica ($P_{SiO} < P_{SiO}^{R_1}$). Section (B): Neck growth kinetics with stabilized silica ($P_{SiO} < P_{SiO}^{R_1}$). Position of samples a, b and c, and samples a*, b* and c* sintered at 1225, 1260 and 1315 °C.

(A) If the effective partial pressure of silicon monoxide at the sample surface is less than the equilibrium partial pressure of SiO from reaction (R_1), $P_{SiO}^{R_1}$ [10], the silica layer is reduced. Neck growth kinetics is given in the section (A) of the diagram where surface diffusion (s(nd) non-densifying mechanism) controls the neck growth rate at all temperatures and neck to particle size ratio. This leads to grain coarsening without densification as experimentally observed in a previous paper [7].

(B) If the effective partial pressure of silicon monoxide at the sample surface is equal to $P_{SiO}^{R_1}$, the silica layer is stabilized. Neck growth kinetics is given in the section (B) of the diagram. Surface diffusion is then strongly slowed down by the presence of the silica layer at the silicon particle surface. Lattice diffusion from the grain boundary (l(d), densifying mechanism) and from the surface (l(nd) non-densifying mechanism) dominate sintering kinetics at high temperature in the early stage of sintering, while vapor transport (v(nd) non-densifying) dominates at low temperature and in the late stage of sintering. Since lattice diffusion from the grain boundary (l(d)) can play a significant role, higher

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