Thermochimica Acta 623 (2016) 65–71

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Isoconversional kinetics of thermal oxidation of mesoporous silicon

Ali Ghafarinazari[a,b,*], Emanuele Zera[c], Anna Lion[d], Marina Scarpa[d], Gian Domenico Sorarù[c], Gino Mariotto[a,b], Nicola Daldosso[a,b]

[a] School of Natural and Engineering Sciences, Nanoscience and Advanced Technologies, University of Verona, Strada le Grazie 15, 37134 Verona, Italy
[b] Department of Computer Science, University of Verona, Strada le Grazie 15, 37134 Verona, Italy
[c] Department of Industrial Engineering, University of Trento, Via Mesiano 77, 38123 Trento, Italy
[d] Laboratory of Nanoscience, Department of Physics, University of Trento, Via Sommarive 13, 38123 Trento, Italy

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 15 October 2015
Accepted 23 November 2015
Available online 2 December 2015

Keywords:
Mesoporous silicon
Model-free kinetics
Model fitting kinetics
Thermal oxidation
Thermogravimetry
Crystallography

ABSTRACT

Mesoporous silicon (pSi) has several interesting features that makes it suitable for various biomedical applications. In particular, the large surface area make it very sensitive to environment changes. Among other approaches, thermal oxidation is an effective way to passivate its surface. Herein, we present experimental and analytical results concerning kinetics of thermal oxidation reaction of pSi. The experiments were conducted on pSi powders produced from silicon wafer by anodization and converted to particles by sonication. Oxidation experiments were carried out at different heating rates. Structure and morphology of the samples have been investigated by XRD and SEM before and after thermal oxidation. The model-free kinetics proposed by Ozawa–Flynn–Wall (OFW) was used to determine the Arrhenius relationship for the pSi thermal oxidation. The obtained apparent activation energy by OFW was confirmed by Starink method. At low temperature, the oxidation of surface dangling bonds obeys the Avrami–Erofeev mechanism. At high temperature, oxidation is followed by classical bulk oxidation according to diffusion mechanism controlled by the diffusion of oxygen through the silicon dioxide layer on the surface of the pSi. The reaction mechanism was checked by the model fitting kinetics, which confirmed the reaction is a kind of sequential two-stage process, Avrami–Erofeev and 3D diffusion. Finally, differential thermal analysis suggests that the second oxidation step is also possibly affected by phase transformation of the silicon dioxide.

1. Introduction

Mesoporous silicon (pSi) possesses some specific properties like biocompatibility, photoluminescence and non-immune response, which makes it a promising material for biomedical applications [1]. Due to its large surface area and highly reactive surface functional groups, pSi is particularly susceptible to air, water, or chemical oxidation [2]. This oxidation has side effects of redox in the biological systems such as tissues [3], proteins [4], and drugs [5]. Nowadays, partial thermal oxidation of pSi has been suggested to solve this issue [6].

Thermal oxidation has been extensively employed by the microelectronic industry to produce high-quality oxides on silicon, and this approach also works with pSi [7]. Noticeably, the rate of oxidation of pSi is greater than that of flat bulk silicon due to the porous structure. The oxidation conditions can be tuned to obtain materials with different properties. Up to now, a variety of effects of oxidation on properties of pSi has been investigated, such as photoluminescence [8,9], biodegradability [10], phonon thermal conductivity [11], and surface reactivity [12]. However, there are only few preliminary reports about thermal oxidation mechanism of pSi [13–15]. For instance, Pep et al. [13] reported that thermal oxidation of pSi consists in two separated steps as a function of the temperature but without any further information and discussion about the kinetic mechanism and the modeling.

In this work, we performed a comprehensive study, both experimental and theoretical, on thermal oxidation of pSi by model-free kinetic (MFK) and model fitting to determine oxidation mechanism. In the case of MFK, OFW (Ozawa–Flynn–Wall) methodology has been used to estimate the kinetic triplet (E, A, and $f(\alpha)$); the obtained E values were confirmed by Starink method. Moreover, model fitting has been applied to find the best kinetic model to disclose the mechanism of thermal oxidation in pSi. The understanding of the oxidation process and the relative mechanism is an important result for basic research on porous materials and also for applicative purposes, mainly in microelectronic and biomaterials fields.

---

[*] Corresponding author. Tel.: +39 388 6598606.
E-mail address: ali.ghafarinazari@univr.it (A. Ghafarinazari).

http://dx.doi.org/10.1016/j.tca.2015.11.017
0040-6031/

2. Experimental procedure

The porous silicon samples have been prepared by anodizing n-type Si (1 0 0) wafers with a resistivity of 0.01–0.02 Ω cm, Sb doped, in a HF (48%), water and Triton X-100 solution (25:200:1). The current density was kept constant at 15 mA cm^{-2} and the etching time was 10 min. The porosity of the samples obtained under these experimental conditions was determined by gravimetric analysis [16] and was found 74 ± 8%. The porous layer was detached from the bulk silicon and fragmented into micro particles by 20 min sonication at 400 W delivered in 80 mL hexane sample volume. Then, the micro particle suspension was centrifuged at 500 × g for 5 min, the surnatant was discarded, the micro particles were dried under gentle nitrogen flow and used within few hours.

X-ray diffraction (XRD) patterns were measured with a D8 Advance Bruker diffractometer, equipped with a Göbel mirror using Cu-$K_{\alpha 1}$ radiation at 1.5406 Å. The patterns were collected with a scan rate of 0.04°/s in the 8°–90° 2θ range. In order to enhance both background and small peak signals, square root of intensity has been illustrated. The crystallite phases were then identified using the Joint Compounds Powder Diffraction Standards (JCPDS) database.

Morphological characteristics have been investigated by scanning electron microscopy with a FE-SEM Zeiss supra 60. The accelerating voltage was 2 kV. The samples were sputtered with gold to assure sufficient conductance.

The simultaneous thermal analyses (STA; i.e. differential thermal analysis (DTA) and thermogravimetry (TG) analysis) were done in synthetic air atmosphere from room temperature to 1273 K with STA 409 (Netzsch–Gerätebau GmbH, Selb, Germany). The STA were conducted at three different heating rate values: 3, 6, and 10 K/min with a flow of 50 mL/min, under ambient atmospheric pressure up to 1273 K. Then, the sample was cooled to room temperature by the rate of 10 K/min. The powder samples, about 20 mg, were kept in alumina crucibles.

A direct way to monitor oxidation phenomenon is TG measurement [13]. The mass variation from TG analysis is correlated to a conversion (α) value by Eq. (1):

$$\alpha_i = \frac{m_s - m_i}{m_s - m_f} \tag{1}$$

where m_s is the starting mass and m_f is the mass after the oxidation. Reaction kinetic can be evaluated by the kinetic triplet (A, E, and $f(\alpha)$) in the kinetic equation expressed in the form of the Arrhenius relationship:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot f(\alpha) \tag{2}$$

Values of the Arrhenius parameters (E and A) are accepted as providing the height of the energy barrier for reaction to occur (the activation energy, E) and the frequency of occurrence of reaction configuration that may lead to product formation (the frequency factor, A). Hence, the reaction model, $f(\alpha)$, represents the dependence on the conversion extent.

The best methodology to evaluate the kinetic triplet (E, A and $f(\alpha)$) is the MFK approach for all kind of reactions [17,18]. Ozawa, Flynn and Wall (OFW) adapted this method to the TG analysis [19,20] and the obtained procedure was validated by the American Society for Testing and Materials (ASTM) for differential scanning calorimetry (DSC) analysis [21]. In summary, integration of Eq. (2) and Doyle approximation [19] leads to:

$$\text{Ln}(\beta) = \text{Ln}\left(\frac{A \cdot E}{R}\right) = \text{Ln}\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) - 5.330 - 1.052\frac{E}{RT} \tag{3}$$

where β is the heating rate. According to Eq. (3), plotting of Ln(β) as function of $1/T$ at different α led to straight lines with slope equal to $-1.052E/R$. The apparent activation energy at the different conversion degree can be calculated from these slopes. Moreover, under the condition of constant α ($\text{Ln}\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) = 0$), by introducing in Eq. (3) the calculated E value, and plotting Ln(β) versus $1/T$, we can estimate the value of Ln(A) [22].

Table 1
Reaction types and corresponding type of $f(\alpha)$ [17].

Model notation	Reaction type	$f(\alpha)$
F_n	nth order (n = 1–3)	$(1-\alpha)^n$
C_n	nth order autocatalysis (n = 1–3)	$(1+K_{cat}\alpha)\times(1-\alpha)^n$
A_n	Avrami–Erofeev (n-D nucleation; n = 1–3)	$n\times(1-\alpha)\times[-\ln(1-\alpha)]^{(1-1/n)}$
D_1	1D diffusion	0.5α
D_2	2D diffusion	$[-\ln(1-\alpha)]^{-1}$
D_3	Jander 3D diffusion	$1.5(1-\alpha)^{2/3}\times[1-(1-\alpha)^{1/3}]^{-1}$
D_4	Ginstling–Brounshtein 3D diffusion	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
R_n	Reaction on the n-D interface (n = 2, 3)	$n\times(1-\alpha)^{(1-1/n)}$
B_{na}	Prout–Tompkins nth order autocatalysis	$(1-\alpha)^n\times\alpha^a$

Moreover, Starink [23] proposed another equation (Eq. (4)) to estimate the oxidation kinetic in a more accurate way.

$$\text{Ln}\left(\frac{\beta}{T^{1.92}}\right) = \text{Ln}\left(\frac{A \cdot E}{R}\right) = \text{Ln}\left(\int_0^{\alpha} \frac{d\alpha}{f(\alpha)}\right) - 1.0008\frac{E}{RT} \tag{4}$$

In this case, plotting Ln($\beta/T^{1.92}$) versus $1/T$ leads to the apparent activation energy. We implemented this method and compared the results with those obtained by OFW method. Therefore, $f(\alpha)$ can be estimated by inserting E and A values in Eq. (2). The kinetic triplet can be derived without any assumption or approximation. By these outcomes, mechanism and kinetics of the oxidation mechanism can be investigated.

Beside to MFK, Model-fitting method is the conventional way to estimate the reaction model ($f(\alpha)$) [24]. In this method, initially, the conventional models (Table 1) were implemented to obtain the best fit model [17]. For each model, the goodness of the fit is customarily estimated by a coefficient of linear correlation (r). A single pair of E and A is then commonly chosen as that corresponding to a reaction model that gives rise to the maximum absolute value of the correlation coefficient [25]. However, this pair of E and A does not have physical meaning. At the end, the obtained model ($f(\alpha)$) has been compared with $f(\alpha)$ estimated by OFW.

Finally, differential thermal analysis (DTA) is performed with identical thermal cycles to obtain an indication of the enthalpy change associated to the reactions (exothermic or endothermic) [4]. This technique helps to define the critical temperatures of the oxidation steps.

3. Results and discussion

The structure and the morphology of pSi samples were investigated by both XRD and SEM. XRD patterns of the as-anodized sample (pSi) and of the sample after heating at 3 K/min up to 1273 K (pSiO_2) are shown in Fig. 1, top and bottom panel, respectively. Formation of single crystalline silicon nanostructure in pSi sample was confirmed (fit to the JCPDS file 27-1402). Indeed, the Bragg condition is only satisfied for ⟨4 0 0⟩ reflection peaked at $2\theta = 69.13°$, according to Ogata et al. [26]. The broad peak at low angles (i.e. 15°–30°) is associated to the amorphous silica [27], probably due to surface oxidation of the silicon crystallites during the sonication. The interface between the oxidized layer and the silicon core is amorphous silicon in the order of ppm, thus not appreciable [28,29]. Moreover, on the pSi surface there are functional groups such as