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A quantitative stress-related model for the evolution of the pore size in porous silicon during high temperature annealing

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Abstract

An original two dimensional model for the simulation of structural pore evolution post-high temperature annealing of porous silicon is proposed. The model treats the pore as a group of vacancies and deals with their diffusion in crystalline materials under mechanical stress. A coupled solution of the mechanical and diffusion field equations is carried out numerically using finite element method. It is found that the pore shape evolution upon annealing at high temperature is essentially dependent on the initial strain created by the pore. The proposed model provides a theoretical basis for the determination of the critical initial pore radius that determines whether the pore will increase or decrease in size upon annealing. Such a critical radius is found to be dependent on the annealing temperature and is calculated for the range 700–1300 °C.

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1. Introduction

Porous silicon (PS) films are being extensively investigated for application in silicon solar cells as anti-reflection coatings (ARC) and as a diffusing back reflector for optical trapping in thin film silicon cells [1–5]. The resulting porous silicon film is characterized by an initial pore size and shape. The initial shape, however, is not permanent since the pore structure might considerably change during subsequent high temperature processing. Attempts have been made to simulate the change of morphology of PS upon high temperature processing based on classical sintering theory [6,7]. In addition, structural changes in PS multilayers during high temperature treatments have been studied experimentally [8]. Quantitative prediction of this evolution is essential to design specific technological steps in order to optimize device performance. In the present work a simplified two dimensional model that predicts the shape of the pore after being treated thermally is proposed. The model is based on the study of diffusion of vacancies in mono-crystalline silicon under the influence of mechanical forces acting on them during high temperature annealing. The model provides a theoretical stress-related explanation for the existence of an initial critical radius that will determine whether the pore will grow or shrink after being subjected to a high temperature treatment, and allows the determination of such a critical radius as a function of the annealing temperature.

2. The model

2.1. Basic description

The proposed model considers a two dimensional planar test cell of undoped mono-crystalline silicon including a single pore. The third dimension, the thickness of the

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porous film, is assumed to be much larger than the pore size (1 μm). The pore is considered to be made from a group of vacancies forming a continuum in the silicon network with the same concentration as the missing silicon atoms. During high temperature treatment, the continuum is under the effect of two mechanisms namely (1) the mechanical forces acting on it, and (2) the vacancy continuity or diffusion mechanism. The target is to determine the modified pore shape from the final vacancy distribution post-high temperature treatment. The governing equations of the forces in both fields are interrelated and therefore a coupled solution must be worked out.

2.2. Mathematical formulation

2.2.1. Mechanical field

During the high temperature treatment three mechanical field stresses act on the vacancies: (1) stress resulting from the pore existence (vacancy relaxation stress), (2) thermal expansion stress and (3) creep stress. These forces are governed by the quasi-static equilibrium differential equation with zero body forces which is given by the divergence of the stress tensor expressed as

$$\nabla \cdot \sigma = 0, \tag{1}$$

where σ is the Cauchy stress tensor. It is more convenient to express σ in a matrix form as

$$\sigma = K\varepsilon_{\mathrm{e}},$$
$$\sigma = K(\varepsilon - \varepsilon_{\mathrm{th}} - \varepsilon_{\mathrm{c}}) + \sigma_0, \tag{2}$$

where K is the 4×4 elasticity matrix made of the effective elasticity modulus terms K_{ij} [9], ε_{e} is the elastic strain matrix obtained from the total strainε diminished by the inelastic thermal strain $\varepsilon_{\mathrm{th}}$ and inelastic creep strain ε_{c} and σ_0 is the initial residual stress resulting from the inelastic vacancy relaxation strain. Eq. (1) should hold at every point in the domain of interest from the mathematical point of view and is subject to the Dirichlet and Neumann boundary conditions [10] given by

$$u(x) = u(x_0) \quad \text{and} \quad \sigma(x)n(x) = r(x_0),$$

i.e. the value of the displacement vectors u at the left hand side is known at a specific point (x_0) at the domain boundary. In these boundary conditions, $n(x)$ is the outward unit vector normal to the surface, and $r(x)$ is the traction vector acting on the interface.

The residual stress σ_0 is caused by strain relaxation in the bonds resulting from vacancy insertion only, and hence is a function of the number of vacancies in the cell. Its dependence on other factors that might affect its value such as dislocations, crystal orientation, grain boundaries, multiple pore distribution, etc. is neglected. The effect of doping will be briefly discussed in this paper. According to the two dimensional model considered here the number of vacancies and hence the residual stress are proportional to the square of the pore radius. In terms of vacancy concentration, the initial vacancy relaxation strain is given by

$$\varepsilon_{\mathrm{v}} = V_{\mathrm{vac}}(C_{\mathrm{v}} - C_{\mathrm{vo}}), \tag{3}$$

where V_{vac} is the volume of the vacancy, C_{v} is the vacancy concentration per unit volume inside the pore and C_{vo} is the vacancy concentration at thermodynamic equilibrium and zero stress. Values for C_{vo} in silicon are available in the literature as a function of temperature [11]. The corresponding ε_{v} tensor is obtained by multiplying ε_{v} with the second-order isotropic tensor I. The thermal expansion strain $\varepsilon_{\mathrm{th}}$ is given by

$$\varepsilon_{\mathrm{th}} = \alpha(T - T_0), \tag{4}$$

where α is the coefficient of linear thermal expansion of silicon [12], T is the absolute temperature, T_0 is a reference temperature (0 °C). The thermal strain tensor is obtained by multiplying $\varepsilon_{\mathrm{th}}$ with the second-order isotropic tensor I.

Creep strain relates to deformation due to vacancy generation or recombination and is relevant only if there are sources or sinks for vacancies, such as dislocations, grain boundaries, as well as when annealing is performed under high gas pressure. The creep strain is not active and will be neglected here since we deal with pores created in an ideal mono-crystalline silicon lattice.

2.2.2. Diffusion field

With no generation or recombination of vacancies, the vacancy diffusion is governed by the continuity equation expressed as

$$\frac{\partial C_{\mathrm{v}}}{\partial t} = -\nabla \cdot j_{\mathrm{v}}, \tag{5}$$

where j_{v} is the vacancy flux. Eq. (5) is subject to the Neumman and Dirichlet boundary conditions [10] given by

$$C_{\mathrm{v}}(x,0) = C_{\mathrm{v}}(x_0), \quad C_{\mathrm{v}}(x,t) = C_{\mathrm{v}}(x_0,t),$$
$$j_{\mathrm{v}}(x,t) \cdot n(x) = j_{\mathrm{v}}(x_0,t)$$

in which the value of the functions at the left hand side are known at a specific point (x_0) at the domain boundary. The vacancy flux j_{v} can be expressed, in terms of the gradient of the vacancy chemical potential μ_{v}, as

$$j_{\mathrm{v}} = -(D_{\mathrm{v}}C_{\mathrm{v}}/kT)\nabla\mu_{\mathrm{v}}, \tag{6}$$

where D_{v} is the temperature dependent diffusivity [11], and k is Boltzman constant. The vacancy chemical potential is defined locally and given by

$$\mu_{\mathrm{v}} = \mu_{\mathrm{veq}} + \frac{\partial g}{\partial C_{\mathrm{v}}}, \tag{7}$$

where μ_{veq} is the equilibrium value of the chemical potential and g is the Gibb's free energy induced due to the addition of a new vacancy while keeping the temperature, the number of atoms and the stress constant. The procedure for calculating the vacancy chemical potential μ_{v} is similar to the technique used in the case of vacancy diffusion in solids and described in detail in [13].