Oxygen redistribution during diffusion in thin silicon layers

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Abstract

During diffusion processes in thin solid layers, the usual assumption of a semi-infinite solid with constant bulk concentration is not valid. The well-known solution of the diffusion equation, based on complementary error functions, is therefore not applicable, and numerical solutions are normally used. In this work, we report an analytical solution for impurity redistribution by diffusion in thin layers. We compare the results of an explicit application of this analytical solution to oxygen out-diffusion in silicon-on-oxide structures with the experimental data, and discuss the limits of its applicability.

Keywords: Diffusion; Oxygen; Silicon; Thin films

1. Introduction

In the study of mass diffusion processes in solids, the most common textbook example is that of impurity diffusion in a semi-infinite sample. The analytical solution, in terms of complementary error functions [1], is well known. However, the assumptions on which this solution is based are frequently not met. One such instance occurs when the solid medium is thin, so that the assumption of a constant concentration of the diffusing species, far from the boundary, is no longer valid. Such a case is becoming more and more frequent, as interest in thin solid layers has grown.

In this work, we report an analytical solution to the diffusion equation for a thin layer, where constant bulk concentration does not exist.

2. Method of approach

We assume, at the beginning of the process, a constant impurity concentration along the whole thickness of the sample (C_B), with surfaces at $x = L$ and $x = -L$, subjected to the same boundary conditions. Two different cases are considered.

(1) Rate-limited case

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0 \tag{1a}$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=L} = h(C_S - C_\infty) \tag{1b}$$

where h is a mass transfer coefficient and C_∞ is the concentration outside the layer (e.g. in the atmosphere).

(2) Diffusion-limited case

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0 \tag{2a}$$

$$C(L) = C_i \tag{2b}$$

where C_i is a fixed impurity concentration at the interface. The first boundary condition, common to both cases, follows from our restriction to symmetrical boundaries.

We search for solutions to Fick's second law, inspired by similar situations found in heat conduction problems [2,3]. In terms of the dimensionless variables (defined for case (1))

$$C^* = \frac{C(x,t) - C_\infty}{C_B - C_\infty} \tag{3a}$$

$$x^* = x/L \tag{3b}$$

$$t^* = \frac{Dt}{L^2} = \mathrm{Fi} \tag{3c}$$

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the diffusion equation becomes

$$\frac{\partial^2 C^*}{\partial x^{*2}} = \frac{\partial C^*}{\partial \mathrm{Fi}} \tag{4}$$

The initial and boundary conditions become

$$C^*(x^*,0) = 1 \tag{5a}$$

$$\left.\frac{\partial C^*}{\partial x^*}\right|_{x^*=0} = 0 \tag{5b}$$

$$\left.\frac{\partial C^*}{\partial x^*}\right|_{x^*=1} = -\mathrm{Bi}C^*(1,t^*) \tag{5c}$$

where $\mathrm{Bi} = hL/D$ is another dimensionless parameter. The solution is

$$C^*(x^*,\mathrm{Fi},\mathrm{Bi}) = \sum_1 A_n \exp(-\xi_n^2 \mathrm{Fi})\cos(\xi_n x^*) \tag{6}$$

with

$$A_n = \frac{4\sin\xi_n}{2\xi_n + \sin(2\xi_n)}$$

and ξ_n the solution of the transcendental equation

$$\xi_n \tan\xi_n = \mathrm{Bi} \tag{7}$$

The solution for case (2) is obtained by setting $h = \infty$ and $C_\gamma = C_i$.

We tested Eq. (6) by comparing the results for short times and large thicknesses with the known solution [1] for out-diffusion in a semi-infinite medium (note that there is a factor of 2 missing in the expressions of Smits and Miller [1] for the impurity concentration in pages 65 and 67 of Ref. [4]) and, for the more general case, with a numerical solution (see Fig. 1) with $L = 200$ μm.
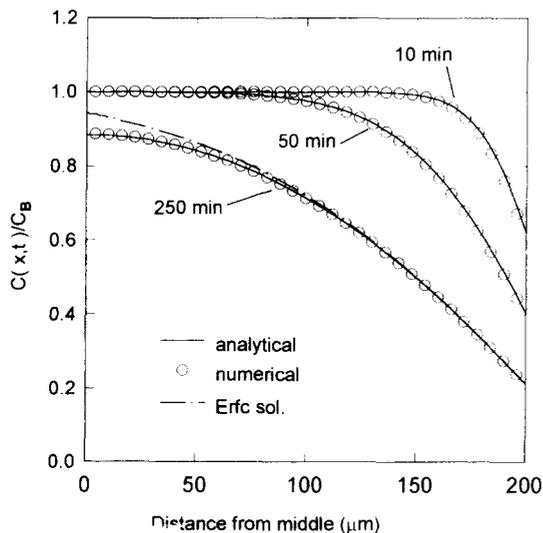

Fig. 1. Comparison between analytical and numerical solutions for the impurity profile at different evolution times using a rate-limited boundary (case (1)) for $L = 200$ μm, $h = 50$ μm h^{-1} and $D = 4.8 \times 10^{-9}$ cm^2 s^{-1}. The results using the analytical solution for semi-infinite solids are also shown.
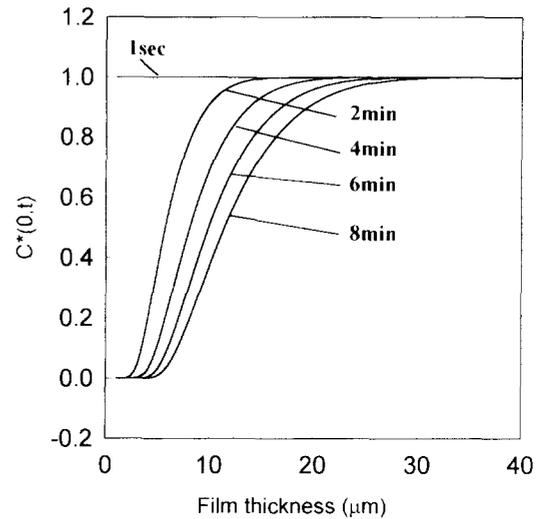

Fig. 2. Oxygen concentration in the middle of the layer vs. layer thickness for different diffusion times just below the melting point.

$h = 50$ μm h^{-1}, $D = 4.8 \times 10^{-9}$ cm^2 s^{-1} (a value indicated by Wilkes [5] for the diffusivity of oxygen in silicon at 1400 °C) and the boundary conditions of case (1). The numerical solution was obtained with a locally developed simulation program using finite-difference methods and Gauss–Seidel iteration [6]. In both cases, the agreement is excellent.

3. Application to oxygen denudation in silicon films

The analysis presented above can be applied to describe the oxygen denudation effect in thin silicon layers. In Fig. 2, we plot the oxygen concentration in the middle of the layer vs. the layer thickness for several diffusion times. The calculations were performed assuming zero oxygen concentration in the atmosphere, $D = 4.8 \times 10^{-9}$ cm^2 s^{-1} and the boundary conditions of case (2). We conclude that, for out-diffusion times of a few minutes, an overall reduction of the oxygen concentration will be noticeable in thin layers.

Such thin films are found in silicon-on-insulator (SOI) structures, and to compare our results with experimental data we used the values reported by Mertens et al. [7] obtained by secondary ion mass spectrometry (SIMS). The SOI structure consists of a silicon layer sandwiched between two thick oxide layers supported by a wafer. The silicon layer is recrystallized (with melting) in a scanning halogen lamp furnace.

The solidification is sufficiently fast such that the silicon layer retains an oxygen concentration equal to its solubility limit at the solidification temperature. Subsequent annealing (holding for 2 min at 1300 °C) of the oxide encapsulated solid layer leads to oxygen out-diffusion towards the silicon–oxide interface. The solubility limit of oxygen in silicon at this lower temper-

ature will impose the oxygen concentration at the Si–SiO_2 interface (case (2)).

In these calculations, we used the same temperature-dependent diffusion coefficient of oxygen in silicon [8] as Mertens et al. [7] ($D = 0.13\exp(-2.53\ eV/kT)$ cm^2 s^{-1}) and the equilibrium oxygen concentration [8] $C_{solub} = 9 \times 10^{22}\exp(-1.52\ eV/kT)$ atoms cm^{-3}, where k is the Boltzmann constant and T is the temperature (K).

We present in Fig. 3 a comparison between the theoretical and experimental profiles obtained in SOI films. The disagreement near the boundaries of the upper curve, and in the lower curve, demonstrates the limits of applicability of the proposed solution. This disagreement is caused by additional diffusion during cooling with a rampdown of 2.5 °C s^{-1}. The lower equilibrium concentration at the interface, combined with the lower diffusion coefficient at the lower temperatures, produces a stronger deviation near the boundaries [6,7]. The proposed analytical solution is therefore especially useful when the integrated effect of cooling (or heating) is small compared with that of the holding time at a constant temperature.

For a constant annealing time and temperature, the oxygen concentration in the middle of the layer decreases as the film thickness decreases, as can be seen in Fig. 4. The theoretical calculations indicated in Fig. 4 (full and broken lines) were performed using the proposed analytical solution with the boundary conditions of case (2). The full line refers to a calculation using the conditions reported by Mertens et al. [7] (2 min at 1300 °C) and the broken line represents calculations for a time of 1 s at 1300 °C.

Fig. 4. Oxygen concentration in the middle of the layer vs. silicon layer thickness. The square symbols for layers with thicknesses of less than 100 μm are SIMS data given by Mertens et al. [7]. Above 100 μm, the squares represent concentration values obtained by IR spectroscopy [9]. The triangle represents an experiment using scanning laser recrystallization [10]. The full line represents calculations using the conditions reported by Mertens et al. [7] (2 min at 1300 °C) and the broken line represents calculations for a time of 1 s at 1300 °C.

In the scanning laser experiments performed by Drowley and Kamins [10] on oxide encapsulated float zone silicon wafers (see Fig. 4), the short time of melting is sufficient to saturate silicon with oxygen. When this layer solidifies, its temperature falls so rapidly that there is negligible oxygen redistribution. Our calculations predict this effect for diffusion times up to a few seconds at 1300 °C, which certainly overestimates the integrated diffusion during cooling.

4. Conclusions

For diffusion processes in thin layers, the usual semi-infinite solid approximation is no longer valid. An analytical solution for the diffusion equation, applicable to such cases, is presented. This solution describes the impurity redistribution due to diffusion in thin layers with good accuracy when the diffusion coefficient can be taken as constant during the annealing process. When the integrated diffusion during the cooling or heating steps is not negligible compared with that during the annealing time, significant deviations can be expected, particularly near the boundaries.
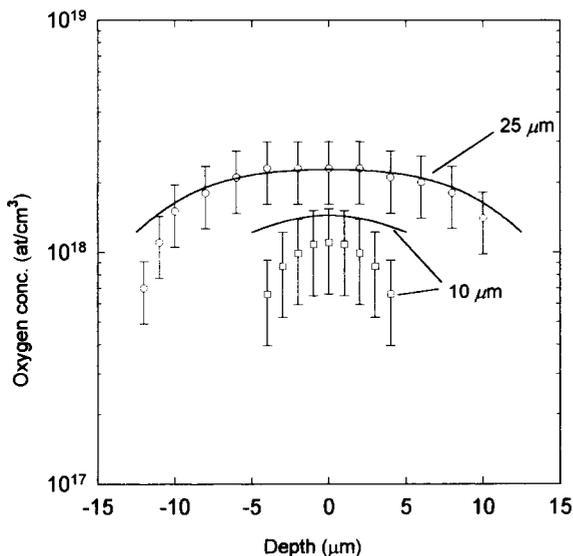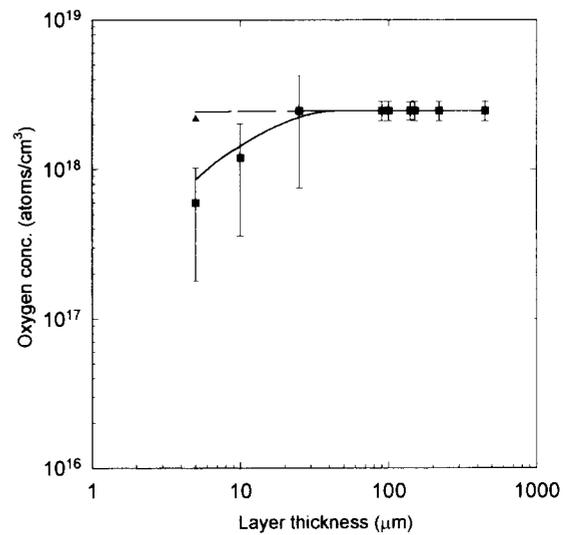

Fig. 3. Measured oxygen profiles in SOI layers with thicknesses of 10 and 25 μm. Full curves are calculations for the reported conditions given by Mertens et al. [7] (2 min holding time at 1300 °C).

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