



UNIVERSITÀ
DEGLI STUDI
FIRENZE

FLORE

Repository istituzionale dell'Università degli Studi di Firenze

On a diffusion problem arising in nanophased thin films

Questa è la Versione finale referata (Post print/Accepted manuscript) della seguente pubblicazione:

Original Citation:

On a diffusion problem arising in nanophased thin films / A.CORLI; V.GUIDI; M. PRIMICERIO. - In: ADVANCES IN MATHEMATICAL SCIENCES AND APPLICATIONS. - ISSN 1343-4373. - STAMPA. - 18:(2008), pp. 517-533.

Availability:

This version is available at: 2158/373324 since:

Terms of use:

Open Access

La pubblicazione è resa disponibile sotto le norme e i termini della licenza di deposito, secondo quanto stabilito dalla Policy per l'accesso aperto dell'Università degli Studi di Firenze (<https://www.sba.unifi.it/upload/policy-oa-2016-1.pdf>)

Publisher copyright claim:

(Article begins on next page)

ON A DIFFUSION PROBLEM ARISING IN NANOPHASED THIN FILMS

ANDREA CORLI

Department of Mathematics, University of Ferrara
Via Machiavelli 35, 44100 Ferrara, Italy
(andrea.corli@unife.it)

VINCENZO GUIDI

Department of Physics, University of Ferrara
Via Saragat 1/c, 44100 Ferrara, Italy
(vincenzo.guidi@unife.it)

MARIO PRIMICERIO

Department of Mathematics “Ulisse Dini”, University of Florence
Viale Morgagni 67/a, 50134 Florence, Italy.
(primicer@math.unifi.it)

Abstract. The selective-sublimation processing is a technique for deposition of thin films. The method consists of the deposition of a solid solution of a mixed-metal oxide with the sublimation temperature of one of the pure metal oxide being rather low. We first model the thermal processing under the assumption that the thickness of the layer is constant. Then, we propose a more general model taking into account the thinning of the film. It results in a free-boundary value problem at the sublimation surface of the film.

Communicated by Editors; Received xxxxxxxx.

This work has been partly supported by project NANO-SENS of the University of Ferrara.
AMS Subject Classification 35K05, 35K20

1 Introduction

The possibility to manipulate the properties of a nanosized thin film simply through thermal treatment appears to be of widespread interest for material science. Such a possibility was exploited in the past in the case of titania (TiO_2) with the inclusion of transition metals (TMs) such as W and Mo with concentration c [5, 9]. Thin films are deposited onto substrates, which serve as a mechanical support only, and thereby are chosen to prevent atomic diffusion into the substrate. As stimulated by temperature, TM tends to migrate toward the surface and here it may oxidize. If the TM oxide has a sublimation temperature lower than that of titania (as is the case of W and Mo), the oxide may leave the film, in turn depleting the thin film from TM in proximity of the surface. Thus, a concentration gradient is being created and the process of diffusion-sublimation may proceed until the film is spoiled by TM. Indeed, some concentration residual c_∞ may remain in the film, which is assumed to be nearly a constant function of the temperature on the strength of experimental evidences. Diffusion of TM, assisted by sublimation, is the base of a methodology for thin-film preparation referred to as selective-sublimation processing (SSP), whose applications have been discussed in [4, 8].

Distinctive features of SSP is that film evolution under annealing can be predicted by means of solely two physical quantities, i.e., temperature and duration of thermal treatment. This indication suggested that the diffusion equation might be called forward for description of SSP, though for the system under consideration such an approach does not necessarily hold true. In fact, for a nanostructured film, atomic diffusion may be significantly affected by the presence of interfaces and grain boundaries, which are preferential sites for variation of composition and chemical state of atomic species with respect to the bulk of the grains.

However, a model was developed, accounting for diffusion equation and surface sublimation [7]. The model consisted of an inverse diffusion problem with fixed boundaries and its predictions were validated experimentally through the determination of the diffusion coefficient D for W and Mo in titania as a function of the temperature. It is indeed surprising that such an inhomogeneous system as a nanophase can be satisfactorily modelled through a continuum-like approach as the diffusion equation.

Indeed, a number of points had to be addressed yet. First, the concentration of TM was purposely set at few percents, otherwise the fixed-boundary assumption could not be applied. Yet, most interesting applications of the SSP do regard the cases when the TM is present with a concentration level comparable to that of Ti. Second, no indication regarding an estimate of the sublimation rate h was determined in [7]. Determination of the physical quantity h provides a consistency check for experimental results. In fact, as sublimation proceeds with rate h , this evidence should agree with the theoretically expected level for a given compound. In principle, such knowledge may also be useful to determine the oxidation state of TM in the oxide during sublimation.

In the present paper we are concerned with both of these issues. In the next Section 2 we introduce the mathematical model for a fixed-depth layer and sketch briefly the way to construct a solution; we also give information about the dependence of the solution on the parameters of the problem. In Section 3 we deal with the estimates of the sublimation rate h and the diffusion coefficient D by means of additional measurements; such estimates

heavily rely on the explicit solution previously constructed.

In Section 4 we address the case of higher concentrations of TM when the variation of the thickness of the layer is to be taken into account. The corresponding free boundary problem is analyzed and the existence of solutions is proved through the convergence of successive approximations.

We believe that our model relying on diffusion equation with free boundary will provide information over a wide interval of metal proportions and may be a reference for further experimentation on this subject with all parameters within the range of applications for the films.

2 The model with a fixed boundary

Denote by l the thickness of the film and let $x = 0$ denote the plane separating titanium dioxide from the substrate. In principle, during annealing the thickness of the layer will change because of sublimation, originating a free-boundary value problem that will be considered in Section 4. Here we take l as a constant.

We assume that TM diffuses in the layer according to Fick's law, so that

$$c_t = (Dc_x)_x, \quad x \in (0, l), \quad t > 0, \quad (2.1)$$

where D , the coefficient of diffusion, depends in general on the linear concentration c of TM and on the temperature T . More precisely, c represents TM linear mass density divided by the mass of an individual TM atom, or the number of TM atoms per unit length over a unit cross-section.

Concerning the temperature, we should find the thermal field solving the heat equation once the appropriate initial and boundary conditions for T are prescribed. In principle one should also include the effect of latent heat of sublimation so that the problems for T and for c are interlocked. In practical cases, however, (i) heat conduction is much faster than mass diffusion, and (ii) latent heat has a negligible effect on the thermal field. Therefore temperature can be assumed as a given function all over the sample. Moreover, in case of SSP, annealing is performed at a given fixed temperature (that may be different in different experiments), so that we will assume that T is a constant for each experiment. In other cases temperature is varying with time but it remains space-independent.

When considering a fixed-boundary problem, a further simplification is produced by the fact that TM is present at very low concentration, so that D can also be assumed to be independent of c .

The initial concentration is prescribed

$$c(x, 0) = c_o(x), \quad x \in [0, l], \quad (2.2)$$

while the boundary conditions on $x = 0$ and $x = l$ express the impermeability of the substrate and a law for the sublimation rate, respectively. The former is simply

$$c_x(0, t) = 0, \quad t > 0, \quad (2.3)$$

while the latter is expressed by a Robin-type condition

$$c_x(l, t) + h(c(l, t) - c_\infty) = 0, \quad t > 0, \quad (2.4)$$

for $h > 0$. This last condition states that the flux of sublimating material is proportional to the deviation of the surface concentration from an equilibrium concentration $c_\infty \geq 0$. Of course, both h and c_∞ depend on temperature and the experimental situation is such that

$$c_o(x) > c_\infty, \quad x \in [0, l]. \quad (2.5)$$

We normalize the concentration introducing

$$u(x, t) = \frac{c(x, t) - c_\infty}{c_o(0) - c_\infty} \quad (2.6)$$

and set

$$\psi(x) = \frac{c_o(x) - c_\infty}{c_o(0) - c_\infty}. \quad (2.7)$$

We define $Q_{\hat{t}} \equiv (0, l) \times (0, \hat{t})$ for any given $\hat{t} > 0$; the set $C^{2,1}(Q_{\hat{t}})$ is the space of functions u that are continuous together with u_x , u_{xx} , u_t in $Q_{\hat{t}}$. We state the diffusion problem in the usual way:

Problem 2.1 *For fixed $D > 0$, $h > 0$ and for a given $\hat{t} > 0$ find a function $u \in C(\overline{Q_{\hat{t}}}) \cap C^{2,1}(Q_{\hat{t}})$ such that $u_x(x, t)$ is continuous in $[0, l] \times (0, \hat{t}]$ and that*

$$\begin{cases} Du_{xx} - u_t = 0 & \text{in } Q_{\hat{t}}, \\ u(x, 0) = \psi(x), & 0 \leq x \leq l, \\ u_x(0, t) = 0, & 0 < t \leq \hat{t}, \\ u_x(l, t) + hu(l, t) = 0, & 0 < t \leq \hat{t}. \end{cases} \quad (2.8)$$

Problem 2.1 is a classical problem for the heat equation, whose well-posedness is proved e.g. in [6, Ch. 5] and in [1, Cor. 7.2.1] if ψ is continuous in $[0, l]$. The explicit solution is given below since it will be useful for the determination of the physical parameters of the problem. We state first some general remarks.

We note that, by the boundary point lemma (see e.g. [6, Ch. 2, Th. 14] or [3, Th. 2.3]), the extrema of u cannot lie on $x = 0$. Using assumption (2.5), i.e. $\psi(x) > 0$, and the same lemma, we get

$$0 < u(x, t) < \max \psi \equiv M, \quad (x, t) \in Q_{\hat{t}}. \quad (2.9)$$

Incidentally, we note that the linearity of the problem implies that uniqueness can be proved by analogous arguments.

Setting $u_x = w$ and assuming that ψ is continuously differentiable in $[0, l]$, we find

$$\begin{cases} Dw_{xx} - w_t = 0 & \text{in } Q_{\hat{t}}, \\ w(x, 0) = \psi'(x), & 0 \leq x \leq l, \\ w(0, t) = 0, & 0 < t \leq \hat{t}, \\ w(l, t) = -hu(l, t), & 0 < t \leq \hat{t}. \end{cases} \quad (2.10)$$

Note that w is allowed to be discontinuous in $(0, 0)$ and/or in $(l, 0)$ since none of the compatibility conditions was assumed in (2.8) but, looking for bounded solutions, [1, §4.4], we have that w is uniquely determined and

$$\min\left\{\min_{[0,l]}\psi', -hM\right\} \leq u_x(x, t) \leq \max\left\{\max_{[0,l]}\psi', -hm\right\}, \quad (x, t) \in Q_{\hat{t}}, \quad (2.11)$$

where $m \equiv \min \psi$. The asymptotic behavior of u can be deduced from [6, Ch. 6, Th. 4], finding

$$\lim_{t \rightarrow \infty} u(x, t) = 0, \quad \text{uniformly in } [0, l]. \quad (2.12)$$

As a consequence $\lim_{t \rightarrow \infty} c(x, t) = c_\infty$. An alternative proof of (2.12) can be obtained by the classical “energy” method.

We briefly discuss now the dependence of the solution of Problem 2.1 on the parameters l and h ; for sake of simplicity we confine ourselves to the case $\psi = 1$. We make the change of variables $\xi = \frac{x}{l}$, $\tau = \frac{tD}{l^2}$; for $v(\xi, \tau) = u(x, t)$ and $\hat{\tau} = \frac{\hat{t}D}{l^2}$, $\alpha = lh$ thus obtaining

$$\begin{cases} v_{\xi\xi} - v_\tau = 0 & \text{in } (0, 1) \times (0, \hat{\tau}), \\ v(\xi, 0) = 1, & 0 \leq \xi \leq 1, \\ v_\xi(0, \tau) = 0, & 0 < \tau \leq \hat{\tau}, \\ v_\xi(1, \tau) + \alpha v(1, \tau) = 0, & 0 < \tau \leq \hat{\tau}. \end{cases} \quad (2.13)$$

We denote by v_α the solution of (2.13); of course we still have $0 < v_\alpha(\xi, \tau) < 1$ for $(\xi, \tau) \in (0, 1) \times (0, \hat{\tau})$. We fix two parameters $0 < \alpha_1 < \alpha_2$; the function $w = v_{\alpha_1} - v_{\alpha_2}$ solves

$$\begin{cases} w_{\xi\xi} - w_\tau = 0 & \text{in } (0, 1) \times (0, \hat{\tau}), \\ w(\xi, 0) = 0, & 0 \leq \xi \leq 1, \\ w_\xi(0, \tau) = 0, & 0 < \tau \leq \hat{\tau}, \\ w_\xi(1, \tau) + \alpha_1 w(1, \tau) = (\alpha_2 - \alpha_1)v_{\alpha_2}(1, \tau), & 0 < \tau \leq \hat{\tau}. \end{cases}$$

By the boundary point lemma we deduce $w(\xi, \tau) > 0$ for $(\xi, \tau) \in (0, 1) \times (0, \hat{\tau})$; therefore v_α is a monotone decreasing function of α . By the same lemma we deduce that $w(\xi, \tau) \leq \frac{\alpha_2 - \alpha_1}{\alpha_1}$, i.e. the continuous dependence of v_α on α . Summing up, in $(0, 1) \times (0, \hat{\tau})$ we have

$$0 < v_{\alpha_1} - v_{\alpha_2} < \frac{\alpha_2 - \alpha_1}{\alpha_1}, \quad \text{for } \alpha_1 < \alpha_2. \quad (2.14)$$

Other estimates come out by considering the function $z(\xi, \tau) \doteq v(1 - \xi, \tau)$; it satisfies

$$\begin{cases} z_{\xi\xi} - z_\tau = 0 & \text{in } (0, 1) \times (0, \hat{\tau}), \\ z(\xi, 0) = 1, & 0 \leq \xi \leq 1, \\ z_\xi(0, \tau) - \alpha z(0, \tau) = 0, & 0 < \tau \leq \hat{\tau}, \\ z_\xi(1, \tau) = 0, & 0 < \tau \leq \hat{\tau}. \end{cases} \quad (2.15)$$

Again we have $0 < z < 1$ in $(0, 1) \times (0, \hat{\tau})$ but now the extrema of z are assumed on $\xi = 0$. To estimate z from above we introduce the function

$$Z_\alpha(\xi, \tau) = \operatorname{erf}\left(\frac{\xi}{2\sqrt{\tau}}\right) + e^{\alpha\xi + \alpha^2\tau} \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}} + \alpha\sqrt{\tau}\right)$$

which satisfies

$$\begin{cases} Z_{\xi\xi} - Z_\tau = 0 & \text{in } (0, +\infty) \times (0, +\infty), \\ Z(\xi, 0) = 1, & 0 \leq \xi < +\infty, \\ Z_\xi(0, \tau) - \alpha Z(0, \tau) = 0, & 0 < \tau < +\infty. \end{cases}$$

From the boundary point lemma we have, for $(\xi, \tau) \in (0, 1) \times (0, \hat{\tau})$,

$$z(\xi, \tau) < Z(\xi, \tau). \quad (2.16)$$

An estimate of z from below is obtained as follows. From (2.16) we deduce $z(0, \tau) \leq e^{\alpha^2\tau} \operatorname{erfc}(\alpha\sqrt{\tau})$ and from the boundary condition we obtain $z_\xi(0, \tau) \leq \alpha e^{\alpha^2\tau} \operatorname{erfc}(\alpha\sqrt{\tau}) \doteq F_\alpha(\tau)$. Consider then the problem

$$\begin{cases} W_{\xi\xi} - W_\tau = 0 & \text{in } (0, 1) \times (0, \hat{\tau}), \\ W(\xi, 0) = 1, & 0 \leq \xi \leq 1, \\ W_\xi(0, \tau) = F_\alpha(\tau), & 0 < \tau \leq \hat{\tau}, \\ W_\xi(1, \tau) = 0, & 0 < \tau \leq \hat{\tau}. \end{cases}$$

The function W_α solving the problem above can be constructed by series expansion, [2], and by the boundary point lemma we deduce

$$W_\alpha(\xi, \tau) \leq z(\xi, \tau). \quad (2.17)$$

We summarize what we found in the following

Proposition 2.2 *Under the previous notation, the solution u_h of Problem 2.1 with $\psi = 1$ corresponding to the parameter h satisfies*

$$0 < u_{h_1} - u_{h_2} < \frac{h_2 - h_1}{h_1}, \quad \text{for } 0 < h_1 < h_2, \quad (2.18)$$

$$W_{lh}\left(\frac{l-x}{l}, \frac{tD}{l^2}\right) \leq u_h(x, t) \leq Z_{lh}\left(\frac{l-x}{l}, \frac{tD}{l^2}\right). \quad (2.19)$$

3 Determination of observable physical quantities

In this section we discuss the determination of parameters h and D by additional physical measurements. We refer to the case $\psi = 1$ for simplicity. Most of the arguments we use can be duplicated with just formal modifications to cover the general case $\psi \in C^1([0, l])$.

The explicit solution to Problem 2.1 through Fourier series (see e.g. [2, §39] and [7]) can be formally written in the form

$$u(x, t) = \sum_{n=1}^{\infty} \psi_n \cos(k_n x) e^{-k_n^2 D t}, \quad (3.1)$$

where k_n are the positive solutions of

$$kl \tan(kl) = hl \quad (3.2)$$

and

$$\psi_n = \frac{4 \sin(k_n l)}{2k_n l + \sin(2k_n l)}$$

are the Fourier coefficients of $\psi = 1$. We denote $u_n(x, t) = \psi_n \cos(k_n x) e^{-k_n^2 D t}$. Since $(n-1)\pi < k_n l < (n-1)\pi + \pi/2$, for $n = 1, 2, \dots$, it is $|\psi_n| \leq 2/|\cos(k_n l)|$ and the series in (3.1) is uniformly convergent in $[0, l] \times [\tau, +\infty)$ for any $\tau > 0$ (indeed $|u_n(x, t)| \leq 2e^{-k_n^2 D t}$). Therefore

$$\lim_{t \rightarrow \infty} u(x, t) = 0$$

uniformly for $x \in [0, l]$, according to (2.12).

Remark 3.1 We have

$$(-1)^n \psi_n < 0, \quad (-1)^n \cos(k_n l) < 0.$$

It is easy to prove that both sequences $\{\gamma_n\} \doteq \{\psi_n \cos(k_n l)\}$ and $\{|\psi_n|\}$ are decreasing. As a consequence, the sequence $\{u_n(l, t)\}$ is strictly positive and decreasing for every $t > 0$; moreover for any $t > 0$ the sequence $\{u_n(0, t)\}$ has alternate signs and $\{|u_n(0, t)|\}$ is decreasing.

Now, we will show that expression (3.1) can be used to determine h from an additional measurement. In fact it turns out that in experiments, [7], the ratio of top-bottom concentration of TM is a quantity that can be precisely measured. We emphasize that it is important to refer as much as possible to observable physical quantities involving function u and not its derivatives, in order to avoid the introduction of error terms due to numerical differentiation of measured values. Hence the additional information we have is

$$\lambda(t) = \frac{u(l, t)}{u(0, t)}.$$

We have $k_2^2 - k_1^2 \geq \frac{3}{4} \frac{\pi^2}{l^2}$ and

$$k_n^2 - k_1^2 \geq \left((n-1)^2 - \frac{1}{4} \right) \frac{\pi^2}{l^2} \geq \left(n + \frac{3}{4} \right) \frac{\pi^2}{l^2}, \quad \text{for } n \geq 3.$$

If we denote for $t > 0$

$$\varepsilon(t) \doteq e^{-\frac{3}{4} r D t} \left(1 + \frac{e^{-3r D t}}{1 - e^{-r D t}} \right) \leq \frac{e^{-\frac{3}{4} r D t}}{1 - e^{-r D t}}, \quad r = \frac{\pi^2}{l^2} \quad (3.3)$$

we deduce by Remark 3.1

$$u(l, t) \leq u_1(l, t) \left(1 + \sum_{n=2}^{\infty} e^{-(k_n^2 - k_1^2) D t} \right) \leq u_1(l, t) (1 + \varepsilon(t)). \quad (3.4)$$

Hence

$$\frac{u_1(l, t)}{u_1(0, t)} < \lambda(t) < \frac{u_1(l, t) (1 + \varepsilon(t))}{u_1(0, t) + u_2(0, t)}$$

and therefore

$$\lambda_\infty \equiv \lim_{t \rightarrow \infty} \lambda(t) = \cos(k_1 l).$$

Recalling (3.2) we find

$$h = \frac{1}{l} \arccos(\lambda_\infty) \cdot \tan(\arccos(\lambda_\infty)). \quad (3.5)$$

This means that the measurement of λ_∞ allows us to find h and then the sequence $\{k_n\}$.

We are now concerned with the evaluation of the sensitivity of the measurement. We focus on the following values for l and h , which correspond to experimental situations, [7, Table II]:

$$l \sim 2 \cdot 10^{-5} \text{ cm}, \quad h \sim 40 \cdot 10^5 \text{ cm}^{-1}.$$

To be specific, in this case the first three solutions of (3.2) are

$$k_1 \sim 7 \cdot 10^4 \text{ cm}^{-1}, \quad k_2 \sim 21 \cdot 10^4 \text{ cm}^{-1}, \quad k_3 \sim 36 \cdot 10^4 \text{ cm}^{-1}.$$

In order to estimate the relative error $\frac{\Delta h}{h}$ as a function of $\frac{\Delta \lambda_\infty}{\lambda_\infty}$ we need to estimate $\frac{d \ln h}{d \ln \lambda_\infty}$. Figure 1 contains the plots of these functions in the case $l = 2 \cdot 10^{-5} \text{ cm}$; the physical value $h = 40 \cdot 10^5 \text{ cm}^{-1}$ is assumed for $\bar{\lambda}_\infty \sim 0.17$ and we compute

$$\frac{d \ln h}{d \ln \lambda_\infty}(\bar{\lambda}_\infty) \sim -1.1.$$

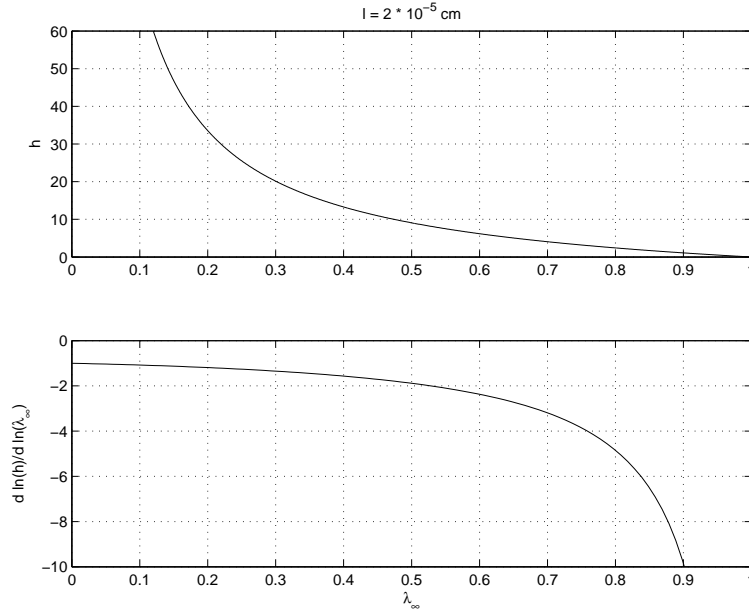


Figure 1: Plots of the functions $h(\lambda_\infty)$ and $\frac{d \ln h(\lambda_\infty)}{d \ln \lambda_\infty}$.

At last, we address to the problem of determining D . From Remark 3.1 we note that $u(l, t) \geq u_1(l, t) = \gamma_1 e^{-k_1^2 D t}$ and then, for every $t > 0$,

$$D \geq \frac{1}{k_1^2 t} \log \left(\frac{\gamma_1}{u(l, t)} \right). \quad (3.6)$$

Remark that k_1 depends only on h and l . We fix now two time values $0 < t_1 < t_2$ and denote by

$$\theta(t_1, t_2) \doteq \frac{u(l, t_2)}{u(l, t_1)}.$$

This is an observable physical quantity. By (3.4) we have

$$\frac{u_1(l, t_2)}{u_1(l, t_1) (1 + \varepsilon(t_1))} \leq \theta(t_1, t_2) \leq \frac{u_1(l, t_2) (1 + \varepsilon(t_2))}{u_1(l, t_1)}.$$

Therefore by the definition of u_1 we deduce

$$-\frac{1}{k_1^2(t_2 - t_1)} \log(1 + \varepsilon(t_1)) \leq D - D^* \leq \frac{1}{k_1^2(t_2 - t_1)} \log(1 + \varepsilon(t_2))$$

for

$$D^* = -\frac{\log \theta(t_1, t_2)}{k_1^2(t_2 - t_1)}.$$

Since $\varepsilon(t_2) \leq \varepsilon(t_1)$ and $\log(1 + x) \leq x$ we get

$$|D - D^*| \leq \frac{1}{k_1^2(t_2 - t_1)} \varepsilon(t_2). \quad (3.7)$$

Formula (3.7) gives an estimate of D in terms of the measurable quantity D^* ; the error term $\varepsilon(t_2)$ can be estimated by the inequality on the right in (3.3) and by (3.6) as

$$\varepsilon(t_2) \leq \frac{\delta^{\frac{3}{4}}}{1 - \delta}, \quad \text{for} \quad \delta = \left(\frac{u(l, t_2)}{\gamma_1} \right)^{\frac{1}{k_1^2} \frac{\pi^2}{l^2}}.$$

4 The free-boundary value problem

Here we adapt our model to the case of higher concentrations of TM. In this case we have to take into account the thinning of the film during the process of sublimation, which is an important issue to be observed and measured in experiments, see [7, Fig. 3]. This means that l cannot be taken as a constant as was the case in Section 2, but it is an unknown function $l = l(t)$ of time whose initial value

$$l(0) = l_o > 0$$

is prescribed (free-boundary value problem); the equilibrium length l_∞ of the film is prescribed as well and we denote

$$R = \frac{l_o}{l_o - l_\infty}.$$

We still assume that D is independent of c .

In order to derive the free-boundary condition on $x = l(t)$ we define

$$N(t) = \int_0^{l(t)} c(x, t) dx.$$

Recalling the definition of $c(x, t)$, we have that $N(t)$ represents the number of TM atoms contained in a cylinder of unit cross-section of the film. We deduce

$$\begin{aligned}\dot{N}(t) &= \int_0^{l(t)} c_t(x, t) dx + c(l(t), t) \dot{l}(t) \\ &= Dc_x(l(t), t) + c(l(t), t) \dot{l}(t).\end{aligned}\quad (4.1)$$

On the other hand we can write

$$l(t) = \mu N(t) + \Lambda$$

where Λ is a constant (the contribution to the width of the film of the TiO_2 atoms) and

$$\mu = \frac{l_o - l_\infty}{c_o l_o - c_\infty l_\infty},$$

so that $\mu N(t)$ measures the contribution of the TM atoms. Remark that $c_\infty \mu < c_o \mu < 1$. Because $\dot{l}(t) = \mu \dot{N}(t)$, by (4.1) we deduce

$$\dot{l}(t) \left(1 - \mu c(l(t), t) \right) = \mu Dc_x(l(t), t). \quad (4.2)$$

We shall prove later on that $c_\infty \leq c(x, t) \leq c_o$ for every $x \in [0, l(t)]$, $t \geq 0$, and then $1 - \mu c(l(t), t) \geq 1 - \mu c_o > 0$. Under (2.6) formula (4.2) writes

$$\dot{l}(t) \left(R - u(l(t), t) \right) = Du_x(l(t), t),$$

which is the free-boundary condition we were looking for. At last, for any $\hat{t} > 0$ define

$$\Omega_{\hat{t}} = \left\{ (x, t) : 0 < x < l(t), 0 < t < \hat{t} \right\}.$$

The aim of this section is to analyze the following

Problem 4.1 *For fixed $D > 0$, $h > 0$ and for a given $\hat{t} > 0$, find a positive function $l(t) \in C[0, \hat{t}] \cap C^1(0, \hat{t}]$ and a function $u \in C(\bar{\Omega}_{\hat{t}}) \cap C^{2,1}(\Omega_{\hat{t}})$ such that u_x is continuous for $x \in [0, l(t)]$, $t \in (0, \hat{t}]$ and that*

$$\begin{cases} Du_{xx} - u_t = 0 & \text{in } \Omega_{\hat{t}}, \\ u(x, 0) = 1, l(0) = l_o & 0 \leq x \leq l_o, \\ u_x(0, t) = 0, & 0 < t \leq \hat{t}, \\ u_x(l(t), t) + hu(l(t), t) = 0, & 0 < t \leq \hat{t}, \\ \dot{l}(t) \left(R - u(l(t), t) \right) = Du_x(l(t), t), & 0 < t \leq \hat{t}. \end{cases} \quad (4.3)$$

Here our aim is not the proof of the well-posedness of a general sublimation problem under minimal smoothness assumptions but we just note the results of this section are easily extended to the case where the condition for $x = 0$ and/or for $t = 0$ are more general.

We deduce now an a priori estimate from below for l . Remark first that by the boundary point lemma we have $u > 0$ in $\Omega_{\hat{t}}$ and $\dot{l}(t) \leq 0$. By applying the Green theorem to the domain Ω_t , $t \leq \hat{t}$, and taking into account the boundary conditions we find

$$l_o + \int_0^t \left[Du_x(l(\tau), \tau) + u(l(\tau), \tau) \dot{l}(\tau) \right] d\tau = \int_0^{l(t)} u(x, t) dx.$$

Since the right-hand side term is positive we deduce $l_o + R(l(t) - l_o) \geq 0$, that is,

$$l(t) \geq \frac{R-1}{R} l_o = l_\infty. \quad (4.4)$$

We begin the analysis of Problem 4.1 by studying an auxiliary problem where $l(t) \in C[0, \hat{t}]$ is a given function satisfying

$$\begin{aligned} l(t) &\geq a > 0 && \text{for } t \in [0, \hat{t}] && \text{and} \\ -L &\leq \frac{l(t_2) - l(t_1)}{t_2 - t_1} \leq 0 && \text{for } 0 \leq t_1 < t_2 \leq \hat{t} \end{aligned} \quad (4.5)$$

while u satisfies (4.3)₁–(4.3)₄. We have

Lemma 4.2 *For every l satisfying (4.5), the solution of the auxiliary problem exists, is unique and satisfies the following inequalities*

$$0 < u < 1, \quad \text{in } \Omega_{\hat{t}}, \quad (4.6)$$

$$0 > u_x > -h, \quad \text{in } \Omega_{\hat{t}}. \quad (4.7)$$

Proof. The well-posedness of the problem is a classical result, see e.g. [1]. The estimates (4.6) and (4.7) are obtained, as in Section 2, by using the maximum principle and the boundary point lemma. Note that, since the data do not satisfy a compatibility condition in $(l_o, 0)$, then u_x is discontinuous at that point. \square

Next, define

$$w(x, t) = u_x(x, t) + hu(x, t), \quad \text{in } \Omega_{\hat{t}}. \quad (4.8)$$

We note that $w(x, t)$ is the unique bounded solution of the problem

$$\begin{cases} Dw_{xx} - w_t = 0 & \text{in } \Omega_{\hat{t}}, \\ w(x, 0) = h, & 0 \leq x \leq l_o, \\ w(0, t) = f(t), & 0 < t \leq \hat{t}, \\ w(l(t), t) = 0, & 0 < t \leq \hat{t}, \end{cases}$$

where we set $f(t) \equiv hu(0, t)$. Moreover $w_x(x, t)$ is known to be continuous for $x \in [0, l(t)]$, $t \in (0, \hat{t}]$.

Proposition 4.3 *For l satisfying (4.5) we have for every $t \in (0, \hat{t}]$*

$$\left| w_x(l(t), t) \right| \leq \frac{2h}{\sqrt{\pi D}} \frac{1}{\sqrt{t}} + K(\hat{t}), \quad (4.9)$$

where $K(\hat{t}) \geq 0$ is a smooth and increasing function

Proof. We denote the fundamental solution for the heat equation

$$\Gamma(x, t; \xi, \tau) = \frac{1}{2\sqrt{\pi D(t-\tau)}} \exp\left(-\frac{(x-\xi)^2}{4D(t-\tau)}\right), \quad t > \tau,$$

then the Green's function for the quarter plane is

$$G(x, t; \xi, \tau) = \Gamma(x, t; \xi, \tau) - \Gamma(-x, t; \xi, \tau).$$

Using Green's identity and Green's theorem and the basic properties of Γ we easily obtain for $t < \hat{t}$

$$\begin{aligned} 0 &= \int \int_{\Omega_t} \left[G(Dw_{\xi\xi} - w_\tau) - w(DG_{\xi\xi} + G_\tau) \right] d\xi d\tau \\ &= \oint \left([DGw_\xi - DwG_\xi] d\tau - Gw d\xi \right) \\ &= D \int_0^t G_\xi(x, t; 0, \tau) f(\tau) d\tau + h \int_0^{l_0} G(x, t; \xi, 0) d\xi \\ &\quad + D \int_0^t G(x, t; l(\tau), \tau) w_\xi(l(\tau), \tau) d\tau - w(x, t). \end{aligned}$$

Differentiating with respect to x we obtain

$$\begin{aligned} w_x(x, t) &= -D \int_0^t N_{\xi\xi}(x, t; 0, \tau) f(\tau) d\tau - h \int_0^{l_0} N_\xi(x, t; \xi, 0) d\xi \\ &\quad + D \int_0^t G_x(x, t; l(\tau), \tau) w_\xi(l(\tau), \tau) d\tau, \end{aligned} \quad (4.10)$$

where we introduced the Neumann function for the quarter plane

$$N(x, t; \xi, \tau) = \Gamma(x, t; \xi, \tau) + \Gamma(-x, t; \xi, \tau),$$

and we used the obvious relationships

$$G_{x\xi} = -N_{\xi\xi}, \quad G_x = -N_\xi.$$

We let now $x \rightarrow l(t)-$ in (4.10); by recalling that w_x is continuous up to the boundary and by using the jump relation for the double-layer heat potential we obtain

$$\begin{aligned} \frac{1}{2} w_x(l(t), t) &= \\ &= D \int_0^t N_\tau(l(t), t; 0, \tau) f(\tau) d\tau - h \left[N(l(t), t; l_0, 0) - N(l(t), t; 0, 0) \right] \\ &\quad + D \int_0^t G_x(l(t), t; l(\tau), \tau) w_\xi(l(\tau), \tau) d\tau. \end{aligned} \quad (4.11)$$

We estimate the term $N_\tau(l(t), t; 0, \tau)$ as follows:

$$\begin{aligned} & \left| N_\tau(l(t), t; 0, \tau) \right| \leq \\ & \leq \frac{1}{2\sqrt{\pi D}} \left\{ \frac{1}{(t-\tau)^{3/2}} e^{-\frac{a^2}{4D(t-\tau)}} + \frac{l_o^2}{2D(t-\tau)^{5/2}} e^{-\frac{a^2}{4D(t-\tau)}} \right\} \end{aligned} \quad (4.12)$$

$$\leq \frac{2\sqrt{D}}{ea^2\sqrt{\pi}\sqrt{t-\tau}} \left\{ 1 + \frac{4l_o^2}{a^2} \right\} \doteq C_1 \frac{1}{\sqrt{t-\tau}} \quad (4.13)$$

by applying the inequalities $xe^{-x} \leq \frac{1}{e}$ and $x^2e^{-x} \leq \frac{2}{e}$, respectively, to the first and the second summand in (4.12). The second summand in (4.11) is estimated by

$$\left| N(l(t), t; l_o, 0) - N(l(t), t; 0, 0) \right| \leq \frac{1}{\sqrt{\pi Dt}} \doteq C_2 \frac{1}{\sqrt{t}}. \quad (4.14)$$

At last

$$\left| G_x(l(t), t; l(\tau), \tau) \right| \leq \frac{L}{4D\sqrt{\pi D}\sqrt{t-\tau}} \left\{ 1 + \frac{2Dl_o}{ea^2L} \right\} \doteq C_3 \frac{1}{\sqrt{t-\tau}}. \quad (4.15)$$

Remark now that $0 \leq f(t) \leq h$ because of (4.6). Then the function $z(t) = |w_x(l(t), t)|$ satisfies an inequality of the type

$$z(t) \leq A + \frac{B}{\sqrt{t}} + C \int_0^t \frac{z(\tau)}{\sqrt{t-\tau}} d\tau$$

for $A = 4Dh\sqrt{\hat{t}}C_1$, $B = 2hC_2$, $C = 2DC_3$. Whence (4.9) follows by Lemma A.2 with

$$K(\hat{t}) = (3A + 4\pi BC)e^{\pi C^2 \hat{t}}.$$

□

Now we define a sequence of successive approximations to Problem 4.1. For $n = 0, 1, \dots$, let u_n solve

$$\begin{cases} Du_{n,xx} - u_{n,t} = 0 & 0 < x < l_n(t), \quad 0 < t < \hat{t}, \\ u_n(x, 0) = 1, & 0 \leq x \leq l_o, \\ u_{n,x}(0, t) = 0, & 0 < t \leq \hat{t}, \\ u_{n,x}(l_n(t), t) + hu_n(l_n(t), t) = 0, & 0 < t \leq \hat{t}, \end{cases} \quad (4.16)$$

where l_n is defined recursively by $l_o(t) = l_o$ and

$$l_{n+1}(t) = l_o - Dh \int_0^t \frac{u_n(l_n(\tau), \tau)}{R - u_n(l_n(\tau), \tau)} d\tau. \quad (4.17)$$

The existence of solutions to (4.16) is guaranteed by Lemma 4.2. Indeed, under the notation of (4.5), one easily proves by induction that every l_n has Lipschitz constant $L \doteq Dh/(R-1)$ in $[0, \hat{t}]$ and, arguing as in the proof of (4.4), the estimate

$$l_n(t) \geq l_\infty \quad (4.18)$$

holds true for $n = 1, 2, \dots$. For any m and n we define for $t \in (0, \hat{t}]$

$$\begin{aligned}\alpha(t) &= \min \{l_m(t), l_n(t)\}, \\ \beta(t) &= \max \{l_m(t), l_n(t)\}, \\ \delta(t) &= \beta(t) - \alpha(t) = |l_n(t) - l_m(t)|.\end{aligned}$$

Remark that α is a Lipschitz function in $[0, \hat{t}]$ with Lipschitz constant $Dh/(R-1)$ and has the same lower bound as both l_m and l_n . We define moreover, for $0 \leq x \leq \alpha(t)$, $0 \leq t \leq \hat{t}$,

$$v(x, t) = u_n(x, t) - u_m(x, t). \quad (4.19)$$

The function v satisfies

$$\begin{cases} Dv_{xx} - v_t = 0 & 0 < x < \alpha(t), \quad 0 < t < \hat{t}, \\ v(x, 0) = 0, & 0 \leq x \leq l_o, \\ v_x(0, t) = 0, & 0 < t \leq \hat{t}, \\ v_x(\alpha(t), t) + hv(\alpha(t), t) = \omega(t), & 0 < t \leq \hat{t}, \end{cases} \quad (4.20)$$

where

$$\omega(t) = \begin{cases} u_{n,x}(l_m(t), t) + hu_n(l_m(t), t) & \text{if } l_m(t) < l_n(t) \\ -u_{m,x}(l_n(t), t) - hu_m(l_n(t), t) & \text{if } l_m(t) > l_n(t). \end{cases}$$

By the boundary point lemma we deduce that $h|v(x, t)| \leq |\omega(t)|$. Moreover we have

$$|\omega(t)| \leq \max_{\alpha(t) \leq x \leq \beta(t)} |w_x(x, t)| \cdot \delta(t) \leq \frac{C^*}{\sqrt{t}} \delta(t) \quad (4.21)$$

because of (4.16)₄, (4.9) and the continuity of w_x up to the boundary. The constant $C^* > 0$ depends on l_∞ , h , D , and \hat{t} .

Fix now $\tau \in (0, \hat{t}]$ and assume $l_m(\tau) < l_n(\tau)$; then

$$\begin{aligned} & \left| u_n(l_n(\tau), \tau) - u_m(l_m(\tau), \tau) \right| \leq \\ & \leq \left| u_n(l_n(\tau), \tau) - u_n(l_m(\tau), \tau) \right| + \left| u_n(l_m(\tau), \tau) - u_m(l_m(\tau), \tau) \right| \\ & \leq h\delta(\tau) + \frac{C^*}{h\sqrt{t}} \delta(\tau). \end{aligned}$$

We estimated the first summand by the mean value theorem together with (4.7), the second one by (4.21). The case $l_m(\tau) > l_n(\tau)$ leads to the same estimate; then

$$\begin{aligned} |l_{n+1}(t) - l_{m+1}(t)| &\leq \frac{Dh}{R-1} \int_0^t \left| u_n(l_n(\tau), \tau) - u_m(l_m(\tau), \tau) \right| d\tau \\ &\leq \frac{D}{R-1} (h^2 t + 2C^* \sqrt{t}) \cdot \max_{\tau \in [0, \hat{t}]} \delta(\tau). \end{aligned}$$

This means that the approximations $\{l_n\}$ converge if \hat{t} is sufficiently small; the limit function l is a $C^1(0, \hat{t})$ function with Lipschitz constant $Dh/(R-1)$. The convergence of the sequence $\{u_n\}$ follows analogously in a standard way by estimating the difference $u_n - u_m$.

It may seem that the argument just shows a local existence, but we note that the constant C^* does not depend on n .

A A Gronwall lemma

We prove in this appendix a Gronwall-type lemma.

Lemma A.1 *Let $T > 0$. Consider two positive functions $\phi(t)$ and $\psi(t)$ which are continuous in $(0, T]$ and satisfy for every $t \in (0, T]$*

$$\phi(t) \leq \psi(t) + \bar{C} \int_0^t \frac{\phi(\tau)}{\sqrt{t-\tau}} d\tau. \quad (\text{A.1})$$

Then for any $t \in (0, T]$

$$\phi(t) \leq \psi(t) + \bar{C} \int_0^t \frac{\psi(\tau)}{\sqrt{t-\tau}} d\tau + \pi \bar{C}^2 \int_0^t \phi(\tau) d\tau. \quad (\text{A.2})$$

Proof. The proof runs as in [1, Lemma 17.7.1], with no need for the assumption that ψ is nondecreasing. We multiply both sides in (A.1) by $(\eta - t)^{-1/2}$ and integrate with respect to t ; then

$$\int_0^\eta \frac{\phi(t)}{\sqrt{\eta-t}} dt \leq \int_0^\eta \frac{\psi(t)}{\sqrt{\eta-t}} dt + \bar{C} \int_0^\eta \frac{1}{\sqrt{\eta-t}} \int_0^t \frac{\phi(\tau)}{\sqrt{t-\tau}} d\tau dt. \quad (\text{A.3})$$

The double integral can be computed by using Fubini's theorem and then making the change of variables $t = \tau + (\eta - \tau)\xi$:

$$\begin{aligned} \int_0^\eta \int_0^t \frac{\phi(\tau)}{\sqrt{\eta-t} \cdot \sqrt{t-\tau}} d\tau dt &= \int_0^\eta \phi(\tau) \left(\int_\tau^\eta \frac{1}{\sqrt{\eta-t} \cdot \sqrt{t-\tau}} dt \right) d\tau \\ &= \pi \int_0^\eta \phi(\tau) d\tau. \end{aligned}$$

The estimate (A.2) follows then by (A.1) and (A.3). □

Lemma A.2 *Assume that for $A \geq 0$, $B \geq 0$, $C > 0$ and $T > 0$ the positive function $\phi = \phi(t)$ is continuous in $(0, T]$ and satisfies for every $t \in (0, T]$*

$$0 \leq \phi(t) \leq A + \frac{B}{\sqrt{t}} + C \int_0^t \frac{\phi(\tau)}{\sqrt{t-\tau}} d\tau.$$

Then for any $t \in (0, T]$

$$\phi(t) \leq \frac{B}{\sqrt{t}} + (3A + 4\pi BC)e^{\pi C^2 t}. \quad (\text{A.4})$$

Proof. We apply Lemma A.1 with $\psi = A + \frac{B}{\sqrt{t}}$, $\bar{C} = C$. We compute easily

$$\int_0^t \frac{\psi(\tau)}{\sqrt{t-\tau}} d\tau = 2A\sqrt{t} + 2\pi B$$

and then (A.2) becomes

$$\phi(t) \leq g(t) + \pi C^2 \int_0^t \phi(\tau) d\tau \quad (\text{A.5})$$

for $t \in (0, T]$ and

$$g(t) = (A + 2\pi BC) + 2AC\sqrt{t} + \frac{B}{\sqrt{t}}.$$

Consider now Gronwall lemma as stated in [1, Lemma 8.4.1]. The proof there is easily extended to cover the case of inequality (A.5), where the function g is unbounded. One obtains then

$$\phi(t) \leq g(t) + \pi C^2 e^{\pi C^2 t} \int_0^t g(\tau) e^{-\pi C^2 \tau} d\tau. \quad (\text{A.6})$$

We make use of the identity

$$\begin{aligned} & (\alpha + \beta\sqrt{t})e^{-\pi C^2 t} + \pi C^2 \int_0^t (\alpha + \beta\sqrt{\tau})e^{-\pi C^2 \tau} d\tau = \\ & = \alpha + \frac{\sqrt{\pi}}{2C}\beta \operatorname{erf}(C\sqrt{\pi t}) \end{aligned} \quad (\text{A.7})$$

for $\alpha, \beta \in \mathbb{R}$, which holds since both sides have the same derivative and coincide at $t = 0$.

The right hand side in (A.6) is easily computed by considering separately the regular part $g_r(t) = (A + 2\pi BC) + 2AC\sqrt{t}$ of g from its singular part $g_s(t) = \frac{B}{\sqrt{t}}$. In fact by (A.7) we get

$$\begin{aligned} & g_r(t) + \pi C^2 e^{\pi C^2 t} \int_0^t g_r(\tau) e^{-\pi C^2 \tau} d\tau = \\ & = \left[A + 2\pi BC + \sqrt{\pi} A \operatorname{erf}(C\sqrt{\pi t}) \right] e^{\pi C^2 t}, \\ & g_s(t) + \pi C^2 e^{\pi C^2 t} \int_0^t g_s(\tau) e^{-\pi C^2 \tau} d\tau = \\ & = \frac{B}{\sqrt{t}} + \pi^{3/2} BC \operatorname{erf}(C\sqrt{\pi t}) e^{\pi C^2 t}. \end{aligned}$$

By estimating $\sqrt{\pi} < 2$ and $\operatorname{erf}(C\sqrt{\pi t}) < 1$ and summing up the previous identities, we obtain (A.4). \square

References

- [1] J. R. Cannon. *The one-dimensional heat equation*, volume 23 of *Encyclopedia of Mathematics and its Applications*. Addison-Wesley Publishing Company Advanced Book Program, Reading, MA, 1984. With a foreword by Felix E. Browder.
- [2] H. S. Carslaw and J. C. Jaeger. *Conduction of Heat in Solids*. Oxford, at the Clarendon Press, 1947.

- [3] A. Fasano. *Mathematical models of some diffusive processes with free boundaries*. Universidad Austral, Rosario, Argentina, 2005.
- [4] M. Ferroni, V. Guidi, G. Martinelli, E. Comini, G. Sberveglieri, A. Vomiero, and G. Della Mea. Selective sublimation processing of a molybdenum-tungsten mixed oxide thin film. *J. Vacuum Sci. Tech. B*, 21:1442–1448, 2003.
- [5] M. Ferroni, V. Guidi, G. Martinelli, and G. Sberveglieri. Microstructural characterization of a titanium-tungsten oxide gas sensor. *J. Material Res.*, 12:793–798, 1997.
- [6] A. Friedman. *Partial differential equations of parabolic type*. Prentice-Hall Inc., Englewood Cliffs, N.J., 1964.
- [7] V. Guidi, G. Martinelli, G. Schiffrer, A. Vomiero, G. Della Mea, E. Comini, M. Ferroni, and G. Sberveglieri. Diffusion-equation approach to describe ionic mobility in nanostructured titania. *Phys. Rev. B*, 72:155401 1–9, 2005.
- [8] V. Guidi, G. Martinelli, G. Schiffrer, A. Vomiero, C. Scian, G. Della Mea, E. Comini, M. Ferroni, and G. Sberveglieri. Selective sublimation processing of thin films for gas sensing. *Sensors and Actuators B*, 108:15–20, 2005.
- [9] G. Sberveglieri, L. Depero, M. Ferroni, V. Guidi, G. Martinelli, P. Nelli, C. Perego, and L. Sangaletti. A novel method for the preparation of nanosized TiO₂ thin films. *Advanced Materials*, 8:334–337, 1996.