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# Laser-induced surface diffusion

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A Brownian motion model for laser-induced surface diffusion is proposed to account for the kinetics of surface transport of the evaporated molecules from a thin discontinuous film under a focused laser beam. The model is solved exactly where the evaporation rate of the molecules is assumed to be proportional to the temperature rise above the ambient of the absorber layer. The surface diffusion constant and molecular velocity are obtained by comparing the results of calculations with transmission electron micrographs of recorded pits in Te trilayer optical discs. These values are in good agreement with Einstein's relation.

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## I. INTRODUCTION

Surface diffusion occurs in various forms of physical phenomena. In field emission microscopy, surface diffusion is studied under controlled conditions where distances on the emitter and time are measurable quantities.<sup>1,2</sup> In other less controlled conditions, such as catalytic reactions or chemisorption processes, usually only the information of average distance and time are available to estimate surface diffusion constants.<sup>3</sup> In those less controlled conditions, surface diffusion is not necessarily restricted to a monolayer of molecules or atoms on the surfaces.

Related to the problems in catalysis are the studies of grain growth in discontinuous thin films. A large amount of work has been devoted to this area.<sup>4-7</sup> Experimental and theoretical efforts have, for the most part, concentrated on the determination of the particle size distribution function and its dependence on substrate and substrate temperature. Typically in discontinuous metal films annealed at temperatures above the deposition temperature the larger grains are observed to grow at the expense of the smaller ones. The resulting particle size distribution has been computed using models for surface diffusion and the transfer of atoms adsorbed on the substrate. Recent developments in the field of optical recording provide another means for studying surface migration. In the case of the trilayer configuration of the optical disc<sup>8</sup> optical absorption occurs in a very thin layer. In some cases the absorber layer is so thin as to be discontinuous as can be seen in the electron micrograph of Fig. 1 provided by McGinn.<sup>9</sup> Here a laser beam approximately one micron in diameter is used to raise the local temperature well above the ambient. Figure 1 suggests that atoms of the absorber layer (Te) have migrated from regions of high temperature and have condensed in the surrounding cooler regions. Thus, the trilayer optical disc provides us a novel means for studying the kinetics of surface transport of atoms of discontinuous films.

In this work we describe the transport in terms of a model in which the elevated temperature creates a surface gas of atoms of the absorber layer on the substrate. This gas then moves from the hot regions of the substrate to the cooler ones, driven by the convective forces of the temperature gra-

dent which are mediated by the interactions of the gas atoms with the local grains and with the substrate. Thus, we have a type of surface diffusion where molecules leave the grains of the discontinuous film at a rate which depends on the intensity of the laser beam and are forced to move outward with an average velocity. When the laser beam is turned off, the molecules recondense with a large density at the outer rim of the focused spot. In optical recordings a "pit" is thus formed. Previously, this pit formation mechanism had been explained by many authors<sup>8,10</sup> as a result of solid melting where surface tension ablates the melting region. However, in the case where the film is very thin and discontinuous, the melting mechanism cannot account for the pit formation. Furthermore, transmission electron micrographs show that there are always small residual solids remaining inside the center region of the pit.

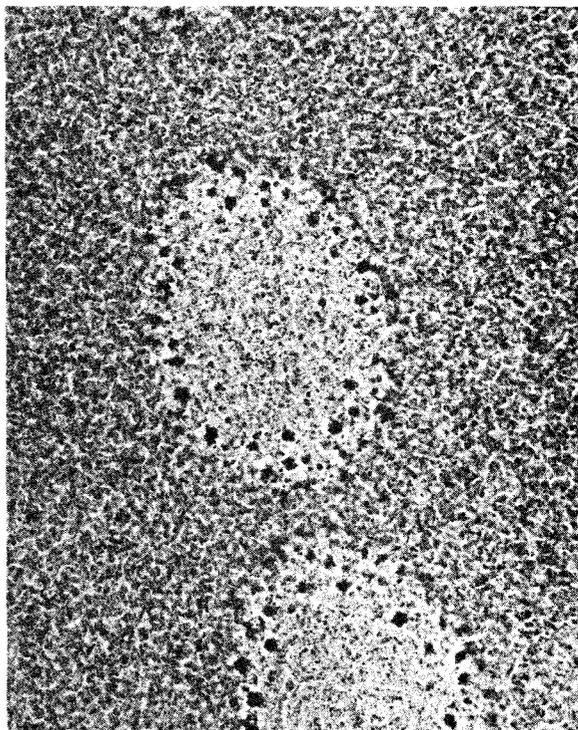


FIG. 1. Transmission electron micrograph of pit structure provided by J. T. McGinn.<sup>9</sup> Note that residual grains (tiny dark spots) exist at the center region of the pit and that the density and size of the grains are much greater near the rim than near the pit center or in the unexposed region. The minor axis of a pit is 0.5  $\mu\text{m}$ .

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Recently, Wobel *et al.*<sup>11</sup> have investigated the laser marking of thin organic films and proposed that the pit formation is caused by laminar flow driven by certain surface forces. In the following, we present this type of surface diffusion as Brownian motion of molecules under an external thermal gradient. Such a model is valid regardless of whether the surface temperature reaches the melting point or not. The evaporation rate of the solid is generally position as well as time dependent since the center of the focused spot receives more photons than the outer area. We approximate this rate by an average value that is time dependent and proportional to the average temperature of the surface. This reduces the complex problem to essentially one dimension where an exact solution can be obtained. The diffusion problem is modeled as if the laser beam is infinitely long in the  $y$  direction, since it will provide the same mechanism of molecular transport if a point-like laser beam is used. It would be difficult to obtain an analytical solution if cylindrical coordinates were used to model the laser spot.<sup>12</sup> The molecular transport can therefore take place in the  $x$  direction, along the surface, and in the  $z$  direction, normal to the surface. As will be shown in Sec. III the average molecular density  $n_1(x,z,t)$  can be expressed as the product of two factors. The surface diffusion factor  $n(x,t)$  is determined by the width of the laser beam ( $\sim 1 \mu$ ), the surface diffusion constant  $D$  and an average drift velocity  $V$ , determined by interactions between the diffusing molecules and the surfaces of the substrate and the grains. The normal,  $z$ -dependent factor is ordinary evaporation and is Gaussian in form.

We first calculate analytically the increase and decrease of surface temperature when a laser beam is incident on the thin film (Sec. II). To account for the space-time distribution of vapors with a given initial distribution, we solve the one-dimensional classical Smoluchowski equation<sup>13-15</sup> exactly with constant velocity where molecules are blocked at the edge of the pit (Sec. III). The exact expression for the vapor density is obtained for the model above. Numerical evaluations of the surface diffusion constant and surface friction coefficient are obtained and are in good agreement with Einstein's relation (Sec. IV).

## II. SURFACE TEMPERATURE

Since we assume that the evaporation rate of molecules is proportional to the temperature rise above the ambient, we would like to evaluate first the time scale of heating and cooling of the thin surface film as compared to the duration of laser pulse. In optical recording, the duration of the laser pulse is set long enough to allow for the steady state of surface temperature to be reached. The nonreflective part of laser power  $P_0$  ( $\text{W}/\text{cm}^2$ ) is absorbed partly by the thin surface film of thickness  $d$ , density  $\rho_1$ , and heat capacity  $c_1$  and remaining power,  $P_0 - \rho_1 \cdot d \cdot c_1 \cdot (dT/dt)$ , is transferred to the second (and transparent) layer through Fourier's law of heat conduction. Thus, we have

$$-K\rho c \frac{\partial T}{\partial z} = P_0 - \rho_1 \cdot d \cdot c_1 \cdot \frac{\partial T}{\partial t}, \quad (1)$$

at the interface between the absorbing film and the second layer. Here,  $K$ ,  $\rho$ , and  $c$  are the thermal diffusivity, density,

and heat capacity of the second layer. Since the laser beam is about  $1 \mu$  in diameter and the second layer may be only about  $750 \text{ \AA}$ , the heat conduction is mainly one dimensional in nature and radial heat flow is negligible (Fig. 2). Thus, the heat flow is governed by

$$\frac{\partial T(z,t)}{\partial t} = K \frac{\partial^2 T(z,t)}{\partial z^2}. \quad (2)$$

The initial position  $z = 0$  is set at the interface of the first and second layers. We further denote the initial (ambient) temperature

$$T(z,0) = T_0, \quad (3)$$

and assume that the third reflective layer is a heat sink; that is,

$$T(l,t) = T_0, \quad (4)$$

where  $l$  is the thickness of the second layer. The heat conduction Eq. (2), along with Eqs. (2), (3), and (4), has been solved numerically by Bartolini *et al.*<sup>8</sup>; here we would like to give an analytical solution.

Let us introduce the following dimensionless position  $\hat{z}$  and time  $\hat{t}$  as

$$\hat{z} = \frac{z}{l} \quad (5)$$

and

$$\hat{t} = \frac{K}{l^2} t, \quad (6)$$

so that the temperature  $T(z,t)$  can be expressed in terms of  $T(\hat{z},\hat{t})$ . Denote the Laplace Transform of  $T(\hat{z},\hat{t})$  as  $\tilde{T}(\hat{z},q)$ ; that is,

$$\tilde{T}(\hat{z},q) = \int_0^\infty T(\hat{z},\hat{t}) \exp(-q\hat{t}) d\hat{t}; \quad (7)$$

then we find  $\tilde{T}(\hat{z},q)$  that satisfies Eqs. (1), (3), and (4) can be written as

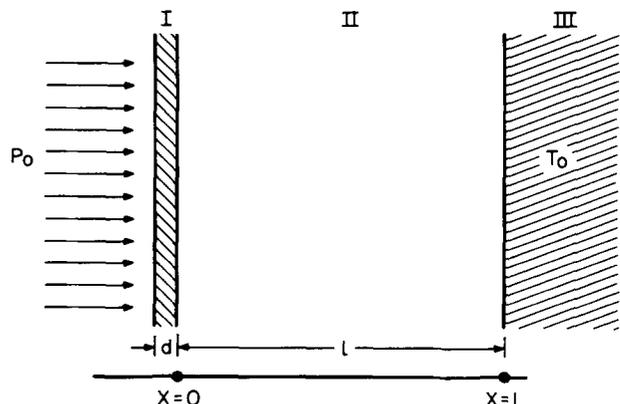


FIG. 2. Laser power  $P_0$  is the incident on a thin discontinuous film of thickness  $d$  (region I, causing the molecules of the grains to evaporate at a rate that is assumed to be proportional to the substrate temperature rise above the ambient. The thickness of the transparent substrate is  $l$  (region II). Laser power is partly absorbed by the thin film being  $\rho_1 d c_1 (dT/dt)$  in region I. The rest of the heat flows into region II. Region III is a reflective layer and is considered a heat sink maintained at temperature  $T_0$ .

$$\bar{T}(\hat{z}, q) = \frac{T_0}{q} - \frac{\beta l^2}{\alpha K q^2} \sinh q^{1/2}(\hat{z} - 1) / \left[ \left( \frac{l}{\alpha} \right) \cdot \frac{1}{q^{1/2}} + \tanh q^{1/2} \right] \cosh q^{1/2}, \quad (8)$$

where  $\beta = P_0/\rho c$  and  $\alpha = \rho_1 d c_1/\rho c$ . The inverse Laplace transform of Eq. (8) can be obtained by summing all the poles located on  $q = 0$  and the negative  $q$  axis, the result is

$$T(\hat{z}, \hat{t}) = T_0 + \frac{\beta l}{K}(1 - \hat{z}) - \frac{\beta l}{K} \sum_i 2 \left( \frac{l}{\alpha} \right) \sin q_i^{1/2}(1 - \hat{z}) \times \exp(-q_i \hat{t}) / \left[ \left( \frac{l}{\alpha} \right) \cos q_i^{1/2}/q_i^{3/2} + \left( \frac{l}{\alpha} \right) \cdot \sin q_i^{1/2}/q_i + \cos q_i^{1/2}/q_i^{1/2} \right] \cdot q_i^2, \quad (9)$$

where the  $q_i$  are positive roots that satisfy

$$\left( \frac{l}{\alpha} \right) \cdot \frac{\cos q_i^{1/2}}{q_i} = \sin q_i^{1/2}. \quad (10)$$

From Eq. (9) we see that the maximum temperature increase at the surface,  $\Delta T_{\max} = T(0, \infty) - T_0 = \beta l/K$ , depends linearly on laser power through  $\beta l/K$ . However, the functional form of the temperature increase depends only on the dimensionless parameter  $l/\alpha$  which is

$$\frac{l}{\alpha} = \frac{\rho_1 l c}{\rho_1 d c_1} \quad (11)$$

or the ratio of products of the density, thickness, and heat capacity of second layer and first layer only.

Experimentally, the first layer is made of a light absorptive tellurium film of thickness  $d \approx 50 \text{ \AA}$  and the second layer is amorphous  $\text{SiO}_2$ , resulting in an  $l/\alpha$  ratio of about 25. The third layer is aluminum. Thus, if laser power  $P_0 \approx 4 \times 10^5 \text{ W/cm}^2$  or  $\beta = 1.9 \times 10^5 \text{ cm deg/s}$  and  $K = 7 \times 10^{-3} \text{ cm}^2/\text{s}$ , then  $\Delta T_{\max} \approx 205 \text{ K}$ . The dimensionless temperature increase  $\Delta T(\hat{z}, \hat{t})/(\beta l/K)$  is plotted in Fig. 3 using the first sixteen roots of Eq. (10). The results are in excellent agreement with those obtained numerically.<sup>8</sup>

The steady state is reached in about 10 ns after which additional laser power is mainly pumped into the aluminum layer. The surface temperature increase  $\Delta T(0, t)$  is shown in Fig. 4, and this temperature determines the evaporation rate of the tellurium film. The threshold power density for the tellurium layer to reach its melting point from  $T_0 = 0^\circ \text{C}$  is

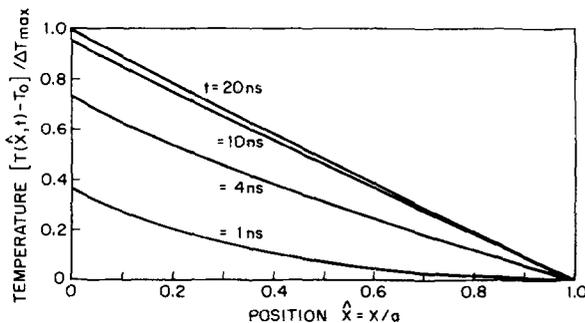


FIG. 3. Temperature increase as function of position and time. The maximum temperature increase is  $\Delta T_{\max} = \beta l/K$  [see text and Eq. (9)].  $l/\alpha$  ratio of 25 is used. Steady state is almost reached at about 10 ns.

$P_0 \approx 8.8 \times 10^5 \text{ W/cm}^2$ . Further increase of laser power would thus shorten the time required to reach the melting temperature. This is shown in Fig. 5.

Experimentally, the duration of laser pulse is about 30 ns while the steady state is reached in 10–12 ns. After the laser pulse is turned off the surface temperature cools off accordingly. The temperature decrease from steady state can be easily calculated by noting that the rates of temperature increase and decrease are the same and that in Eq. (9) the second term and the third term cancel each other at  $t = 0$ . Therefore, the temperature decrease is

$$T(\hat{z}, \hat{t}) = T_0 + \frac{\beta l}{K} \sum_i 2 \left( \frac{l}{\alpha} \right) \sin q_i^{1/2}(1 - \hat{z}) e^{-q_i \hat{t}} / \left[ \left( \frac{l}{\alpha} \right) \cdot \frac{\cos q_i^{1/2}}{q_i^{3/2}} + \frac{l}{\alpha} \cdot \frac{\sin q_i^{1/2}}{q_i} + \frac{\cos q_i^{1/2}}{q_i^{1/2}} \right] \cdot q_i^2, \quad (12)$$

where  $\beta l/K$  is the steady-state temperature. The cooling of surface layer is plotted in Fig. 4. Thus the evaporation rate  $h(t)$  of tellurium molecules under our assumption is

$$h(t) = h \cdot \left[ \frac{\Delta T(0, \hat{t})}{\beta l/K} \right], \quad (13)$$

where  $h$  is the rate at the steady-state temperature. The quantity inside the bracket is dimensionless, as shown in Fig. 4, including heating and cooling of the surface temperature.

### III. SURFACE DIFFUSION AS BROWNIAN MOTION OF MOLECULES

The molecules evaporated from the grains of the film diffuse into the upper half of  $z$  space and we assume that the density  $n_1(x, z, t)$  satisfies

$$\frac{\partial n_1}{\partial t} = D_z \frac{\partial^2 n_1}{\partial z^2} + D \frac{\partial^2 n_1}{\partial x^2} \mp V \frac{\partial n_1}{\partial x}. \quad (14)$$

Uniformity in the  $y$  direction is assumed since we have an infinitely long laser beam. The radical velocity (+ sign for  $x > 0$  and - sign  $x < 0$ ) in  $x$  direction is determined by the convective driving force  $F$ , whose origins lie in the temperature gradient and the effective surface friction coefficient. The diffusion normal to the surface is independent from that in the  $x$  direction and is a Gaussian diffusion process into a free half-space originating at  $z = 0$ . Therefore,  $n_1(x, z, t)$  is factored into

$$n_1(x, z, t) = n(x, t) (\pi D_z t)^{-1/2} \exp(-z^2/4D_z t), \quad (15)$$

where  $z \geq 0$  and  $n(x, t)$  satisfies

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \mp V \frac{\partial n}{\partial x}, \quad (16)$$

the + sign is for  $0 > x \geq a$  and the - sign is for  $-a < x < 0$ , where  $a$  is the radius of the focused spot. Equation (16) is the classical Smoluchowski equation<sup>13–15</sup> that describes the one-dimensional Brownian motion of particles driven by an external force. Since the effect of diffusion in the  $z$  direction is cancelled by that of recondensation when the laser beam is turned off, we need only to consider the quantity  $n(x, t)$ . In

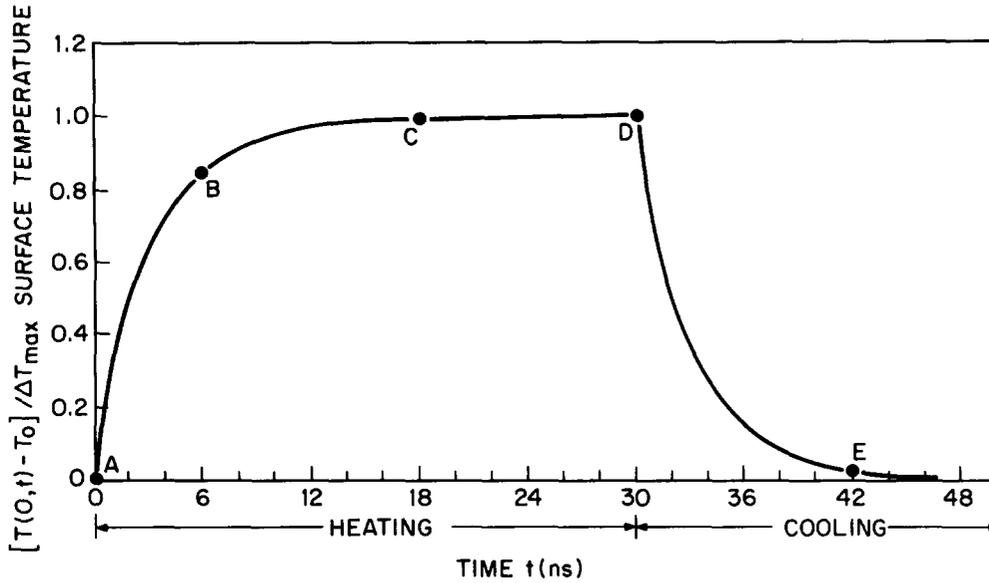


FIG. 4. Surface temperature during the heating process [Eq. (9), up to 30 ns as shown by point D] and cooling process [Eq. (12) evaluated at  $z = 0$ ]. The evaporation rate of molecules  $h(\tau)$  is taken as proportional to the temperature increase of the thin film. Points A, B, C, D, E, are for further reference to Fig. 6 (see text).

addition, it is worth mentioning that the diffusion constant  $D_z$  is rather small as compared to  $D$  in the  $x$  direction since the evaporation takes place at a maximum temperature well below the boiling point of tellurium and therefore with a very low vapor pressure.<sup>16</sup> Let us consider the solution of Eq. (16) with an initial uniform probability density  $n_0 = 1/2a$  and determine the probability density  $n(x,t)$  at position  $x$  and time  $t$ .

At the boundary of the focused spot, we assume that the molecules cease to move so that the molecular flux at the boundary is

$$D \frac{\partial n}{\partial x} \mp V \cdot n = 0 \quad \text{at } x = \pm a. \quad (17a)$$

Similarly, the continuity of flux and density at the origin requires that

$$D \frac{\partial n}{\partial x} - V \cdot n|_{x=0^+} = D \frac{\partial n}{\partial x} + V \cdot n|_{x=0^-}, \quad (17b)$$

and

$$n(0^+) = n(0^-). \quad (18)$$

Equation (16) can be simplified by writing

$$n(x,t) = u(x,t) \exp\left(\pm \frac{Vx}{2D} - \frac{V^2 t}{4D}\right), \quad (19)$$

where  $+$  ( $-$ ) sign applies to upper (lower) sign of Eq. (16). Then  $u(x,t)$  satisfies

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2}. \quad (20)$$

The Laplace transform of Eq. (20), as defined by Eq. (7), is

$$D \frac{\partial^2 u}{\partial x^2} - q \cdot u = -n_0 \cdot \exp\left(\mp \frac{Vx}{2D}\right). \quad (21)$$

It is now convenient to introduce the Green's function  $G(x, x_0, q)$  that satisfies

$$D \frac{\partial^2 G}{\partial x^2} - q \cdot G = \delta(x - x_0), \quad (22)$$

with the same boundary conditions as  $u(x, q)$ . The inverse Laplace transform of  $G(x, x_0, q)$  can then be obtained and written as

$$G(x, x_0, t) = \left[ \frac{-1}{a} \sum_{n=1}^{\infty} \cos \frac{n\pi}{a}(x_0 - x) + \frac{1}{a} \sum_{n=1}^{\infty} \left( \frac{V^2}{4} - \frac{n^2 \pi^2 D^2}{a^2} \right) \cdot \cos \frac{n\pi}{a}(x + x_0) \right] \left/ \left( \frac{V^2}{4} + \frac{n^2 \pi^2 D^2}{a^2} \right) - \frac{V \cdot D}{a^2} \right. \\ \times \sum_{n=1}^{\infty} n\pi \cdot \sin \frac{n\pi}{a}(x + x_0) \left/ \left( \frac{V^2}{4} + \frac{n^2 \pi^2 D^2}{a^2} \right) \right] \cdot \exp\left(-\frac{n^2 \pi^2 D t}{a^2}\right) - \frac{V}{2D} \\ \times \exp\left[-\frac{V}{2D}(a - x_0 - x) + \frac{V^2 t}{4D}\right] \left/ \sinh \frac{Va}{2D} \right. \quad \text{for } 0 < x < a, \quad (23)$$

and the corresponding Green's function  $G(x, x_0, t)$  for  $-a < x < 0$  can be obtained by replacing  $V$  by  $-V$  in Eq. (23). Using  $G(x, x_0, t)$  for Eq. (21) to obtain  $u(x, t)$  and thus  $n(x, t)$  from Eq. (19), we have finally

$$n(x,t) = \left[ \frac{n_0}{2a} \sum_{n=1}^{\infty} \left( \frac{V}{2D} \cos \frac{n\pi x}{a} + \frac{n\pi}{a} \sin \frac{n\pi x}{a} \right) - \frac{n_0}{2a} \sum_{n=1}^{\infty} \left( \frac{V^2}{4} - \frac{n^2 \pi^2 D^2}{a^2} \right) \cdot \left( \frac{V}{2D} \cos \frac{n\pi x}{a} - \frac{n\pi}{a} \sin \frac{n\pi x}{a} \right) \right] \left/ \left( \frac{V^2}{4} + \frac{n^2 \pi^2 D^2}{a^2} \right) \right. \\ + \frac{n_0 V D}{2a^2} \sum_{n=1}^{\infty} n\pi \cdot \left( \frac{V}{2D} \sin \frac{n\pi x}{a} + \frac{n\pi}{a} \cos \frac{n\pi x}{a} \right) \left/ \left( \frac{V^2}{4} + \frac{n^2 \pi^2 D^2}{a^2} \right) \right] \cdot \left[ 1 - (-1)^n \exp\left(-\frac{Va}{2D}\right) \right] \\ \times \exp\left[ \frac{Vx}{2D} - \left( \frac{n^2 \pi^2 D}{a^2} + \frac{V^2}{4D} \right) t \right] \left[ \left( \frac{V}{2D} \right)^2 + \left( \frac{n\pi}{a} \right)^2 \right] + \frac{n_0 V a}{4D} \cdot \exp\left[-\frac{V}{2D}(a - 2x)\right] \left/ \sinh \frac{Va}{2D} \right. \quad (24)$$

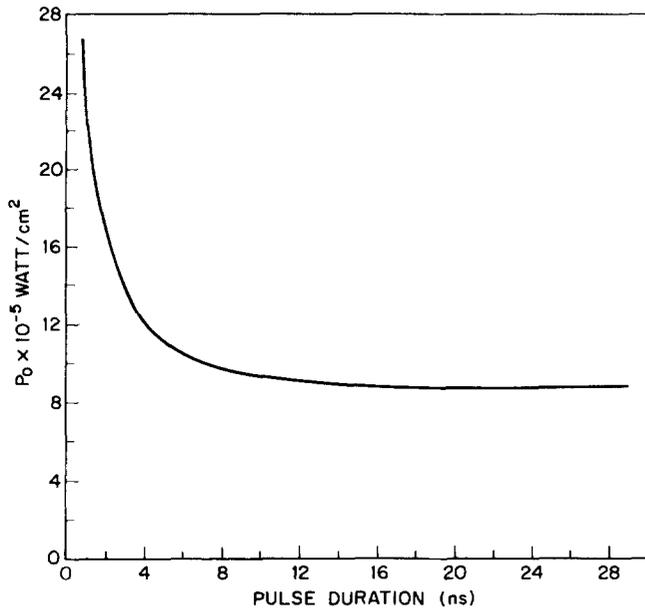


FIG. 5. Laser power densities required to reach the melting point as a function of laser pulse duration. The asymptotic laser power is about  $8.8 \times 10^5$  W/cm<sup>2</sup>. A similar curve is obtained for the power required to reach the boiling point with an asymptotic value of  $1.9 \times 10^6$  W/cm<sup>2</sup>.

By noting that  $n_0 = 1/2a$ , we can show that Eq. (24) satisfies the proper normalization; that is

$$\int_0^a n(x,t) dx = 1/2, \quad (25)$$

and

$$n(x,0) = \frac{1}{2a} \text{ for } 0 < x < a. \quad (26)$$

Similarly  $n(x,t)$  for  $-a < x < 0$  can be obtained by replacing  $V$  by  $-V$  in Eq. (24).

#### IV. TOTAL DENSITY AND NUMERICAL EVALUATIONS

We would like now to apply the exact solution of the probability density  $n(x,t)$  obtained in Sec. III to calculate the total density  $N(x,t)$  of the molecules. Since the molecules are removed from the solid at the rate of  $h(\tau)$  at the time  $\tau$ , the number of molecules contributed to the total density between  $\tau$  and  $\tau + d\tau$  is  $h(\tau)d\tau$ . At a later time  $t$ , after an interval  $t - \tau$ , the Brownian motion of molecules changes the uniform distribution into a new profile which is  $n(x, t - \tau)h(\tau)d\tau$ . After summing all the available times  $\tau$  at time  $t$ , we have the total density  $N(x,t)$  written as

$$N(x,t) = \int_0^t n(x,t - \tau)h(\tau)d\tau. \quad (27)$$

Because the surface temperature is maintained at steady state for most of the duration of the laser pulse, we expect that the evaporation rate  $h(t)$  of the tellurium film will be approximately constant at a certain high rate except during the periods of rapid temperature increase and decrease. Furthermore, although at the ambient temperature, molecules may leave the grains of discontinuous film individually at an Arrhenius rate or the very low evaporation rate, as temperature increases, molecules may not leave individually. In-

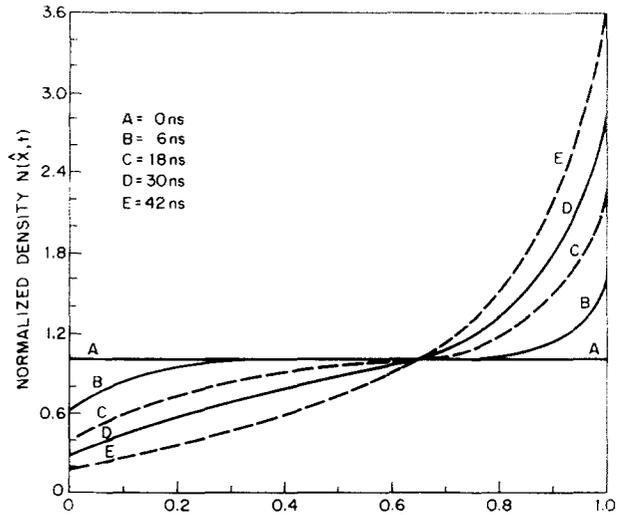


FIG. 6. Total density  $N(\hat{x},t)$  as a function of position and time (nanoseconds). Initially the thin and discontinuous film is statistically uniform as indicated by curve A, where  $n_0 = 1/2a$  is set equal to 1. Curve B indicates a weak pit is formed at 6 ns. Curve C is at 18 ns where maximum surface temperature has already been reached. Curve D is the pit geometry when laser power is turned off at 30 ns. When the surface temperature is cooling off, additional transport takes place until the surface temperature almost reaches the ambient temperature (40 ns). This additional change of pit geometry during the cooling process is significant (see text for the corresponding dimensionless time scales).

stead, clusters of molecules may begin to leave simultaneously from the grains and break up only subsequently. The high evaporation rate therefore implies that layers of molecules peel off simultaneously from the grains and then break up to become individual molecules, each of which acquires high kinetic energy. Thus, due to the large perturbation nature of the laser power used, the evaporation rate is not related to the activation energy that a molecule is associated with but is related to the energy the molecule acquired in the gas state. This leads us to assume that evaporation rate  $h(t)$  is proportional to the temperature rise above the ambient. Thus,  $h(t)$  is given by Eq. (13). The result can be expressed in terms of double sums by noting that

$$\begin{aligned} & \int_0^t d\tau \left\{ \sum_n a_n \cdot \exp[-b_n(t - \tau)] \right\} \cdot \left\{ \sum_i c_i \exp(-q_i \tau) \right\} \\ &= \sum_n \sum_i a_n c_i [\exp(-q_i t) - \exp(-b_n t)] / (b_n - q_i), \end{aligned} \quad (28)$$

where  $a_n$  are the coefficients of  $\exp\left[-\left(\frac{n^2 \pi^2 D}{a^2} + \frac{V^2}{4D}\right)t\right]$  in Eq. (24) and  $c_i$  the coefficients of  $\exp(-q_i t)$  in Eq. (9). The calculation of Eq. (27) is straightforward. However, the final expression is rather lengthy so we will omit it here and give only the numerical evaluations. The results are shown in Fig. 6 in terms of normalized density and dimensionless units as  $N(\hat{x},\hat{t})$  where  $\hat{x}$  and  $\hat{t}$  are dimensionless position and time defined as

$$\hat{x} = \frac{x}{a}, \quad (29)$$

and

$$\hat{t} = \frac{Dt}{a^2}, \quad (30)$$

and

$$N(\hat{x}, \hat{t}) = \frac{\int_0^i n(\hat{x}, \hat{t} - \hat{\tau}) h(\hat{\tau}) d\hat{\tau}}{\int_0^i h(\hat{\tau}) d\hat{\tau}}. \quad (31)$$

The double sums of indices  $n$  and  $i$  [Eq. (28)] are evaluated up to  $n = 40$  and  $i = 16$ , respectively. In those limits, we have very accurate numerical evaluations to show that  $n(x, 0) = (1/2a)$  and  $h(0) = 0$  up to an error of the order of  $10^{-4}$ . The other dimensionless parameter involved in this evaluation is  $R$ , where

$$R = \frac{V \cdot a}{D}. \quad (32)$$

From the steady-state solution [the last term of Eq. (24)], we note that  $R$  also determines the final steady-state profile of the pit formation. However, the  $t \rightarrow \infty$  stage is never reached experimentally, since at  $t \approx 40$  ns (as shown in Fig. 4), the surface temperature returns to room temperature and  $V \approx 0$ . From the transmission electron micrograph, the pit structure falls off exponentially to the  $e^{-1}$  position at approximately  $2/3$ – $3/4$  of the radius. In this way we obtain an estimated value of  $R$ :

$$R \approx 5. \quad (33)$$

The dimensionless time during the heating process is

$$\hat{t}_1 \approx 0.1, \quad (34)$$

and the total time including cooling is

$$\hat{t}_2 \approx 0.14. \quad (35)$$

The corresponding surface diffusion constant  $D$  and velocity  $V$  are

$$D \approx 0.833 \times 10^{-2} \text{ cm}^2/\text{s}, \quad (36)$$

and

$$V = 8.33 \text{ m/s}, \quad (37)$$

using pit radius  $a = 0.5 \mu\text{m}$ . We further evaluate the effective surface friction coefficient  $f$  using Einstein's relation

$$f = 2kT/D, \quad (38)$$

where  $k$  is the Boltzmann constant. With the value of  $D$  given in Eq. (36), we have

$$f \approx 10^{-11} \text{ g/s}. \quad (39)$$

From this, one can check roughly the consistency between the values  $D$  and  $V$  obtained in Eqs. (36) and (37). Let us assume the force per particle due to the temperature gradient is of the order of

$$F = -k \frac{\partial T}{\partial x}. \quad (40)$$

Using  $\Delta T = 500^\circ\text{C}$  over the distance  $\Delta x = 0.5 \mu$ , the corresponding velocity

$$V = F/f \approx 5.55 \text{ m/s}. \quad (41)$$

In Fig. 6, the total density is shown as a function of successive time intervals, where (a) is the initial unperturbed film

( $\hat{t} = 0$ ), (b) at time  $\hat{t} \approx 0.02$ , (c) at  $\hat{t} = 0.06$ , (d) at  $\hat{t} = 0.1$  or the end of the heating process, and (e) at  $\hat{t} \approx 0.14$  or the end of the cooling process. From the difference between curves (d) and (e), we see that after the laser beam is turned off, the next 12 ns of the cooling process have a drastic effect on the profile of final pit geometry.

## V. CONCLUSIONS

We have presented a model for the migration of molecules of the grains of a discontinuous film on a substrate with continuous evaporation rates. The model is one of surface diffusion in the presence of a driving force created by imposed temperature gradients and mediated by interactions between the migrating molecules and the substrate. It is worth noting that our model generalizes the concept of grain growth in discontinuous films. Without the driving force, our model is essentially a continuum model of grain growth so that, while there are fluctuations of grain sizes from one position to another, the density is uniform on the average ( $V \rightarrow 0$  limit). However, when the driving force is activated the average grain size on the outer rim becomes larger while on the inner area it becomes smaller. In the model, the average density takes on a time-varying spatial distribution. The depletion of the center area is then totally due to the existence of such a driving force.

The fitting constants  $D$  and  $V$  obtained have the meaning of diffusion constant and velocity of the Brownian particles driven by a given force in an infinite system. When blocking boundary conditions are imposed, the average diffusion constant  $\bar{D}(t)$  and average velocity  $\bar{V}(t)$  over the pit size will become time dependent even though the corresponding infinite systems are time independent. When steady state is reached, the values of  $\bar{D}(t)$  and  $\bar{V}(t)$  vanish.

The pit formation mechanism so proposed differs from the fluid model and surface-tension model of others in that there is no threshold laser power required to create a pit. The numerical results are quite reasonable, suggesting that the model can provide the physical basis for pit formation, regardless of whether it is a strong or weak pit, in the trilayer optical disc. In addition, the model can provide a means for measuring the parameters governing surface diffusion in discontinuous films for both finite and infinite systems. The study of this example also provides a model for the kinetics of transport of thin macroscopic layers of molecules. This model has many practical applications.

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