# Calculation of thermal emissivity for thin films by a direct method

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(Received 3 March 1997; revised manuscript received 20 October 1997)

The emissivity variation of a body, according to the modifications of its surface, has been described by two kinds of arguments. A direct argument consists in adding the energy, leaving each element of volume $dV$, considered as independent and incoherent Planckian radiators, weighted by its transmissions and its possible reflections. An indirect argument consists in assuming the validity of Kirchhoff's law. The emissivity is then deduced from the absorption coefficient calculated by using a huge collection of theoretical means. However, in the case of very thin films deposited on a substrate, the emissivity calculated according to their thickness does not give the same results, depending on the argument used. As a matter of fact, up to now the direct argument did not allow a description of interferential phenomena. Such phenomena are still observed when the film thickness is lower than, or of the same order of magnitude as the wavelength of the radiation concerned. On the other hand, the use of Kirchhoff's law requires delicate handling in the case of mesoscopical structure materials. Besides, the indirect method leads to an argument by default, which occults a part of the physics implied. Here, a direct model is proposed, only based on emission phenomena. This direct theory allows a description of the interferential behavior in thermal radiation, by taking into account the self-coherence of the emitted waves, in contrast to the previous direct approach. It is shown that this approach accounts for the experimental behavior of growing thin films. [S0163-1829(98)01812-8]

## I. INTRODUCTION

### A. Direct and indirect arguments

The study of the thermal radiation process still remains an interesting topic. It concerns various application fields, such as pyrometry, radiative heat transfer, and more recently, remote sensing or object signature prediction and control. Nowadays, the radiative properties analysis is even considered as a possible and alternative means of *in situ* surface investigation and control during surface treatments. But to develop these kinds of applications, it is necessary to have theoretical models allowing us to calculate the emissivity of the material studied, depending on its physicochemical and structural parameters.

Actually, few theories can describe directly the emissivity of a body, except for black bodies using Planck's radiation law which is a theoretical one, and the fundamental theory on spontaneous and induced emissions using the Einstein coefficients; this is even more true for a real body in real situations. In particular, no theory allows for direct determination of the emissivity of mesoscopical structures, such as multilayers structures, microroughness, microcermet structures used, for instance, in selective absorbant layers, or issues in infrared reflecting materials still studied. More generally, we note that in reference handbooks on optics, the theoretical description of the radiative properties of materials is often particularly succinct.[1]

For the emissivity $\varepsilon$ of a real body, the small amount of theoretical means is certainly due to its definition given with respect to the emissive properties of a theoretical body. On the contrary, many theories describe the reflection, transmission, and absorption coefficients $\rho$, $\tau$, and $\alpha$, according to the physical properties of a material and of its surface, such as reflection and refraction theories, thin films theory, effective medium theory, etc. These coefficients are easy to use: they are simply defined with respect to a chosen primary incident wave.

To circumvent the difficulty linked with its definition, as recently pointed out in a study performed by multiple wavelengths pyrometric interferometry,[2] the emissivity is usually calculated by an indirect argument that transforms an emission problem into a reflection problem.[3–6] It consists in calculating the reflection ($\rho$), transmission ($\tau$), and absorption ($\alpha$) coefficients of the system, in order to determine the emissivity value ($\varepsilon$) by using at the end of the calculation both the conservation energies relation ($\alpha=1-\rho-\tau$) and Kirchhoff's second law ($\varepsilon=\alpha$).

The direct argument is practically unused. It consists in trying to obtain the global radiative behavior of a real body,[7] from the spectral volume emissive power of the matter ($j\lambda$) divided into elements of volume $dV$. The idea was proposed by H. O. McMahon in 1950 (Ref. 8) and developed by R. Gardon in 1956.[9] But this direct model, as already pointed out by A. K. S. Thakur,[10] does not always give the same results as the indirect model [Fig. 1(d)]. Incidentally, among other reasons, this has for a long time fueled controversy on the range of validity of Kirchhoff's law.[11,12] Yet today this law seems well established, at least in the field of linear optics and in the case of elastic scattering, considering the induced emission as negative absorption. This is true even for macroscopic complex systems in nonthermal equilibrium with the surrounding radiation fields, provided the body is considered at uniform temperature (constant or varying very slowly) or more precisely, provided the material quantum states of this body obey the equilibrium distribution, and provided the problems linked with the reflection reciprocity of the materials are taken into account.[11–16]

As a matter of fact, and as we will see later, the McMahon-type direct models are available only for materials

 

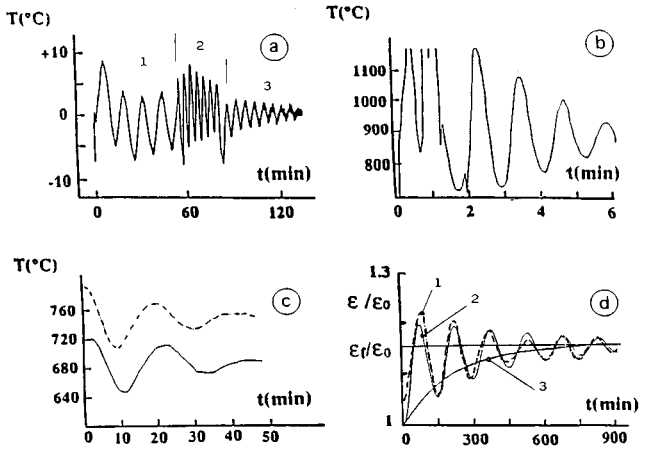


FIG. 1. (a) Apparent temperature oscillation during sequential growth of epitaxial layers of AlAs (1), $Ga_{0.61}As_{0.39}$, As (2), and GaAs on GaAs substrate (3) by A. J. Spring Thorpe *et al.* (Ref. 20). (b) Variation of apparent temperature during deposition of diamond on Mo substrate by K. A. Snail *et al.* (Ref. 21). (c) Apparent temperature measured during deposition of silicon on $SiO_2$ with two deposition rates by R. Buchta *et al.* (Ref. 22). (d) Relative emissivity variation at $\lambda = 2.3\ \mu$m during growth of diamond on silicon substrate by S. Barrat *et al.* (Ref. 23). $\varepsilon_0$ is the clean silicon substrate emissivity at the beginning of the treatement. $\varepsilon_f$ is the emissivity of diamond. 1: Experimental results (dotted line). 2: Usual indirect modeling (periodical solid line) 3: Direct modeling by McMahon method (monotonical solid line).

that are homogeneous and macroscopic. They become unusable in the case of mesoscale structures, for instance, a bulk substrate covered with a thin film whose thickness is inferior to or of the same order of magnitude as the wavelength λ.

Therefore, an indirect argument is mainly used nowadays to determine the emissivity of any real body. But this indirect argument is an argument by default which omits the emission process actually studied. Besides, its use is not always appropriate. In some cases of inhomogeneous materials at a mesoscopical scale, an effective medium cannot be defined, and then the parameters $\alpha$, $\tau$, and $\rho$ cannot be calculated. On the other hand, even when the calculation of the parameters is possible, the use of Kirchhoff's second law is difficult to justify in this range of sizes.

### B. Case of emissivity oscillations during growth of films

Among various application fields, these models are expected to describe the evolution of the optical properties of the surface during its modifications. For instance, thermal radiation fluctuations are experimentally observed during the first steps of the growth of films deposited on substrates (Fig. 1). These fluctuations were first used successfully as a means of controlling surface treatment processes, by Dumin[17] who monitored the growth of Si on sapphire, and by Clark and co-workers[18] who measured the endpoint film thickness (in the case of $Al_2O_3$ deposition on silicon substrate). Later, small, nonuniform variations of spectral and directional radiative power have been observed by IR spectrometric observations, during the first stages of oxide growth on tungsten substrate performed at constant temperature.[5,19] Since then, many similar observations of periodical fluctuations of thermal radiations or more simply of temperatures indicated by a pyrometer, have been made during CVD (chemical vapor deposition) on MWCVD (assisted by microwave) surface treatments (Fig. 1),[20–23] or during molecular-beam epitaxy (MBE) processes.[24]

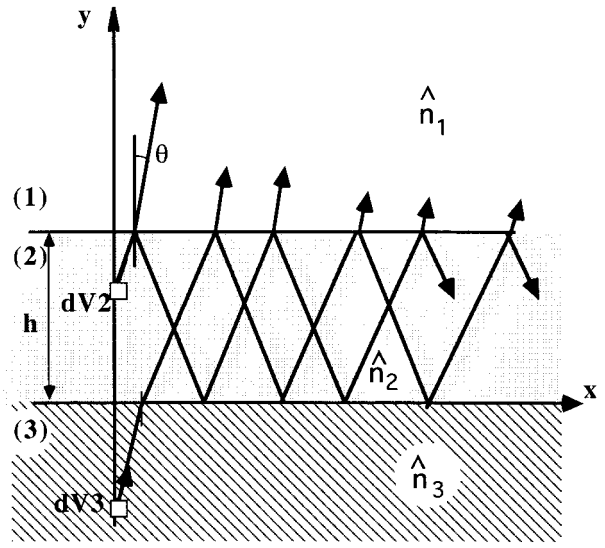


FIG. 2. Radiation emitted by a system composed of a film (2) deposited on a substrate (3).

The interferential nature of these oscillations is now a proven fact. Indeed, we know that the indirect model previously mentioned can describe correctly this nonuniform thermal emission behavior in the simple case of homogeneous deposit.[5,6,22] It allows us to know, *in situ* and in real time, some microscopic surface parameters, and then to follow their evolution during a surface reaction,[23,25] but with the reservations previously expressed.

On the other hand, by using the classic direct method, the calculation of $\varepsilon = f(t)$, for the simple case of a semitransparent thin film growth [thickness equal to $h(t)$] on an opaque substrate, ends up in a monotonic evolution incompatible with the experimental data.[10] Only the initial values $\varepsilon_0 = \varepsilon(t=0)$ and the $\varepsilon(t)$ values for a very thick film are correct [Fig. 1(d)]. They correspond respectively to the emissivity of the clean substrate ($h=0$) and the emissivity of the film material when it is sufficiently thick to be opaque. Therefore, a direct model actually dealing with the emissive phenomenon and able to describe correctly this experimental behavior has surprisingly not been written yet.

In the present paper such a direct model is proposed. It is the counterpart of the usual indirect model, but removes the ambiguity due to the *de facto* application of Kirchhoff's law. It could be an interesting theoretical way to calculate the radiative power of mesoscopical structure materials.

## II. THEORY

### A. Usual direct model (McMahon-type)

Let a system at the uniform temperature $T$ be composed of (a) a substrate (medium noted 3, Fig. 2) with a complex refractive index $\hat{n}_3(T) = n_3 - ik_3$ and sufficiently thick to be considered opaque, (b) a deposited film (medium noted 2,

Fig. 2) with a refractive index $\hat{n}_2 = n_2 - ik_2$ and a thickness $h(t)$. This freely radiating system is in vacuum (medium 1 with $\hat{n}_1 = 1$). Let $e_i(\lambda,T)d\lambda$ be the radiative power per unit volume in the range $\lambda \pm \Delta\lambda/2$ for each medium $(i)$. Each element of volume is considered as an independent source (Planckian radiator) emitting incoherent beams. In order to simplify, all the subsequent arguments will be written out for the normal emergence, $\theta = 0$. The total radiative energy released in **O***y* direction per unit area emerging from the upper surface of the film $(y = h)$ per unit time and unit solid angle is given by integration over the whole volume of the contribution of the radiative power $e_i(\lambda,T)d\lambda$ of each element of volume $dV$ at temperature $T$, in the substrate $(i = 3)$ and in the film $(i = 2)$. Each contribution is the result of the energy coming from each $dV$ simply weighted by the absorption, $\exp(-4\pi k_2 l/\lambda)$ and/or $\exp(-4\pi k_3 l/\lambda)$, along the path $l$ through medium 2 and/or 3 and suffering multiple absorptions and transmissions within the film.[7,26–28]

With Kirchhoff's law,

$$e_2(\lambda,T)/k_2 = e_3(\lambda,T)/k_3 = e(\lambda,T)/k \tag{1}$$

and after integration of all the contributions, the total radiative energy released in **O***y* direction is

$$I(\lambda)d\lambda = \frac{\lambda e(\lambda,T)d\lambda}{4\pi k}\{T_{31}\exp(-4\pi k_3 h/\lambda) + T_{21}[1-\exp(-4\pi k_2 h/\lambda)]\}, \tag{2}$$

where $T_{31}$ and $T_{21}$ are the net intensity transmission coefficients for the interfaces 3/1 and 2/1.[27]

The black body radiations can be expressed as

$$I_0(\lambda)d\lambda = \lambda e(\lambda,T)d\lambda/4\pi k. \tag{3}$$

Thus, the spectral and normal emissivity is usually expressed as [from Eqs. (2) and (3)]

$$\varepsilon_\lambda = I(\lambda)/I_0(\lambda) = \underbrace{T_{31}\exp(-4\pi k_3 h/\lambda)}_{\text{Substrate}} + \underbrace{T_{21}[1-\exp(-4\pi k_2 h/\lambda)]}_{\text{Film}}. \tag{4}$$

The total energy of the system being calculated from incoherent radiations emitted by each $dV$ [Eq. (2)], we can see that when $h$ varies from zero to a thickness equal to the penetration depth, the emissivity [Eq. (4)] varies monotonically from the emissivity $\varepsilon_{31}$ of medium 3 to the emissivity $\varepsilon_{21}$ of medium 2 that has become opaque [as for example on curve 3, Fig. 1(d)].

### B. Indirect model

In an indirect argument for the same system (at uniform temperature $T$), a primary plane wave (with a wavelength equal to $\lambda$) is considered incident under $\theta$ on the upper surface and coming from the vacuum (Fig. 3). With Kirchhoff's law and the energy conservation law, the emissivity under $\theta$ $\varepsilon_{\theta,\lambda,T}$ of this system can be expressed as

$$\varepsilon_{\theta,\lambda,T} = \alpha_{\theta,\lambda,T} = 1 - \rho_{\theta,\lambda,T} \tag{5}$$

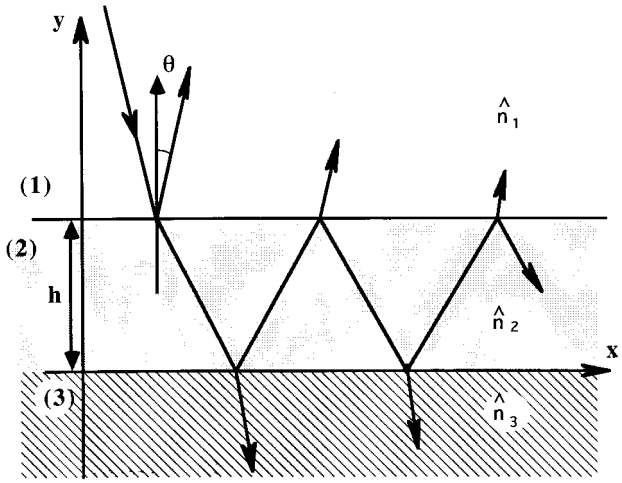


FIG. 3. Reflection of an incident wave on a film-substrate system.

with $\alpha_{\theta,\lambda,T}$ the absorption coefficient, $\rho_{\theta,\lambda,T}$ the reflection coefficient, and a transmission coefficient $\tau_\lambda = 0$ since medium 3 is opaque.

Then for $\theta = 0$ and fixed thickness $h$, the reflection coefficient can be calculated from the thin film theory as

$$\rho_{\lambda,T}(h) = \frac{Ae^{2\alpha_2} + Be^{-2\alpha_2} + C\cos 2\gamma_2 + D\sin 2\gamma_2}{e^{2\alpha_2} + ABe^{-2\alpha_2} + E\cos 2\gamma_2 + F\sin 2\gamma_2}, \tag{6}$$

with

$$\alpha_2 = 2\pi k_2 h/\lambda \quad \text{and} \quad \gamma_2 = 2\pi n_2 h/\lambda, \tag{7}$$

and where $A,B,C,D,E,F$ are different constants depending only on the complex refractive indices of each medium $\hat{n}_2(\lambda,T)$ and $\hat{n}_3(\lambda,T)$, and previously defined.[28]

By this classical method (division of amplitude) the emissivity shows an interferential behavior when the thickness increases, exactly as experimentally observed.[23] Experimental observations of emissivity variations during the film growth performed simultaneously at different wavelengths $\lambda$ have allowed us to confirm the validity of this model.[29] We can show that the maxima and minima experimentally observed on $\varepsilon$ occur at values of $n_2 h$ given, respectively, by (for $n_2 > n_3$ and $n_1 = 1$):

$$n_2 h = (2m+2)\lambda/4 \quad \text{and} \quad n_1 h = (2m+1)\lambda/4, \tag{8}$$

with $m$ integer and inversely for $n_2 < n_3$, $n_1 = 1$. We can show that the damping is proportional to $\lambda/4\pi k_2$.

### C. Direct model of emissivity by division of amplitude method

If the indirect models are incontestable under the restrictions previously mentioned, in fact they occult the thermal emission phenomenon studied. Here, for the same *substrate +film* system as above, each element of volume is considered (as in Sec. II A) as an independent radiative source at given temperature $T$. From this volume $dV$ some waves are emitted in all directions, in the range $\lambda \pm \Delta\lambda/2$.

We assume a volume $dV$ immersed in an infinite body, called medium $(i)$, with *medium/vacuum* interfaces infinitely remote. A unit surface $dS$ at distance $l$ for $\theta = 0$ from $dV$

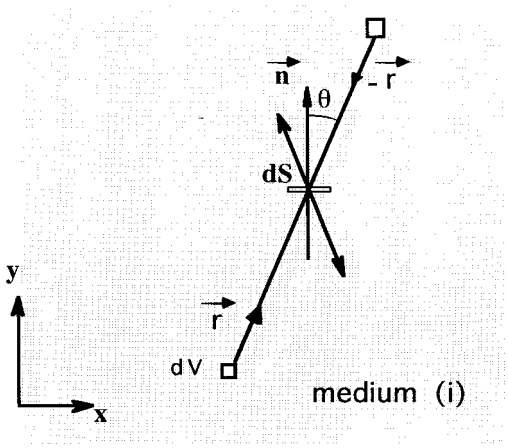


FIG. 4. A surface $dS$ in the bulk of a medium $(i)$ determines two semi-infinite bodies. On each of its sides, this surface $dS$ receives identical radiations from these two bodies.

(Fig. 4) receives a wave emitted from $dV$, here for the electric field and in the direction of propagation $\mathbf{r}$, as

$$E(l)=I_i e^{i\omega t}e^{-i(2\pi l/\lambda)\hat{n}_1}, \tag{9}$$

with $I_i$ the intensity of the wave emitted by $dV$. Under the same direction $\mathbf{r}$, this surface receives from a half space an energy which will be proportional to

$$W_i=\int_{-\infty}^{0}|E(y)|^2dy=\int_{-\infty}^{0}I_i^2e^{-4\pi y k_i/\lambda}dy=\frac{\lambda I_i^2}{4\pi k_i}, \tag{10}$$

with $|E_y|^2=E_yE_y^*$ ($E_y^*$ conjugate-complex of $E_y$).

This surface receives the same energy from the other half space on its other side, under the direction $-\mathbf{r}$. This ''aperture $dS$'' is in thermodynamic equilibrium. It emits in direction $\mathbf{r}$ what it receives under the same incidence. It behaves like a *black body ''cavity aperture''* with $W_i=W_0$, the total radiative intensity of a radiation emitted by a black body, exactly in the same way as a material surface $dS$ had been enclosed in a perfect black body cavity. The Poynting vector of this radiation will be

$$S_i=S_0=\hat{n}_i c W_i/4\pi. \tag{11}$$

#### *1. Refractive index discontinuity influence*

The medium $(i)$ with refractive index $n_i-ik_i$ is now a material half space (Fig. 5). The other half space is another medium (1), for example, the vacuum with refractive index $n_1=1$.

A $dS$ surface taken on the interface $(i)/(1)$ receives from medium $(i)$ on its internal side the previous energy $W_0$, but due to the presence of the refractive index discontinuity, a part of each wave (emitted from each $dV$) is reflected into the medium $(i)$ and only a part of each wave emerges to the upper medium (1). For normal incidence $\theta=0$, the coordinate system shown in Fig. 6, with the specifications $s$ and $p$, respectively, for the perpendicular and the parallel polarization, the Fresnel equations describe the refraction phenomena according to the polarization of the waves, written to simplify as follows for the transmission:

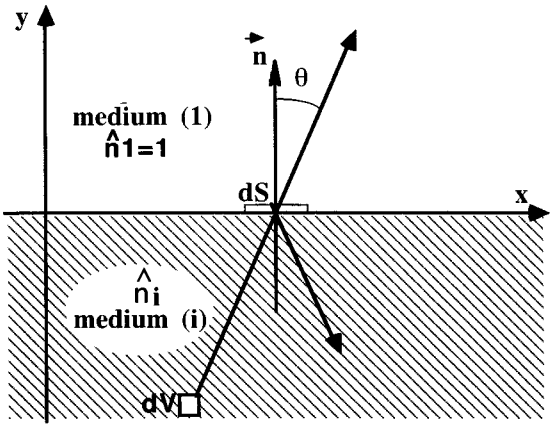


FIG. 5. On an index discontinuity $(1/i)$, a surface $dS$ receives on its internal side (medium $i$) the radiation emitted by each element of volume $dVi$.

$$t_{(i)/1}=t^s_{(i)/1}=t^p_{(i)/1}=\frac{2\hat{n}_i}{\hat{n}_i+\hat{n}_1}, \tag{12}$$

and for the reflection

$$r_{(i)/1}=r^s_{(i)/1}=r^p_{(i)/1}=\frac{\hat{n}_i-\hat{n}_1}{\hat{n}_i+\hat{n}_1}. \tag{13}$$

The internal side of $dS$ receives from medium $(i)$, the substrate, the wave emitted by $dV$ (at distance $l$ and for $\theta=0$)

$$E_i=I_i e^{i\omega t}e^{-i(2\pi l/\lambda)\hat{n}_i}. \tag{14}$$

The part of this wave ''emitted'' in direction $\mathbf{O}y$ by the other side of $dS$ into medium (1) is (for $\theta=0$) as follows:

$$E_i^t=t_{(i)/1}E_i=\frac{2(n_i-ik_i)E_i}{n_i-ik_i+1}. \tag{15}$$

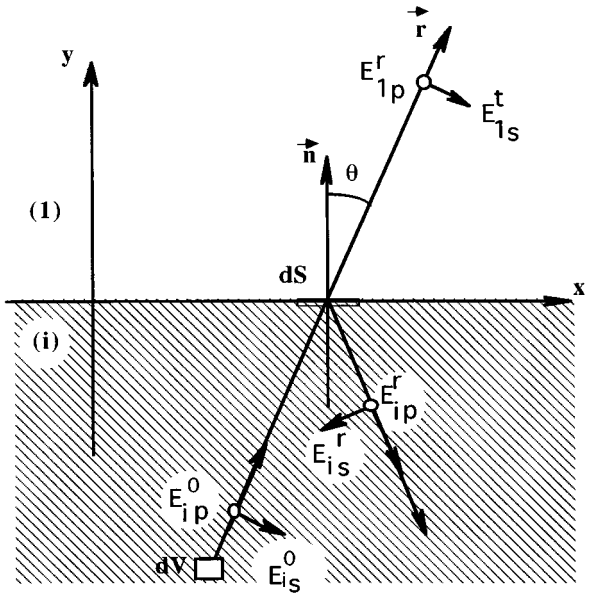


FIG. 6. Orientation of electric fields $Es$ and $Ep$ during reflection and transmission.

The energy of this wave will be proportional to

$$dW_{(i)/1}=|E_i^t|^2=I_i^2 t_{(i)/1}t^*_{(i)/1}e^{-4\pi l k_i/\lambda}. \tag{16}$$

Thus, as above, the energy emitted in direction **O***y* by the medium $(i)$ will be proportional to

$$W_{(i)/1}=\int_{-\infty}^{0}|E_i^t(y)|^2dy=\frac{\lambda I_i^2}{4\pi k_i}\left\{\frac{4[(n_i^2+n_i+k_i^2)^2+k_i^2]}{[(n_i+1)^2+k_i^2]}\right\}, \tag{17}$$

and the Poynting vector of the set of waves will be

$$S_{(i)/1}=\frac{c}{4\pi}\,\hat{n}_1 W_{(i)/1}. \tag{18}$$

The time average of the ratio of the Poynting vectors before and after the transmission will be

$$\left\langle\frac{S_{(i)/1}}{S_i}\right\rangle=\mathrm{Re}\left\{\frac{\hat{n}_1}{\hat{n}_i}\right\}t_{(i)/1}t^*_{(i)/1}=\frac{4n_i}{(n_i+1)^2+k_i^2}=\varepsilon_{i1}, \tag{19}$$

where $\mathrm{Re}\{\hat{n}_1\}$ is the real part of $\hat{n}_1$ and where $S_i$ is the Poynting vector of the set of waves before the transmission [Eq. (11)], and therefore identical to the set of waves emitted by a black body. Equation (19) gives the emissivity $\varepsilon_{i1}$ of the medium $(i)$ measured in medium 1 (i.e., the vacuum). It is the same result as the one obtained by an indirect argument using the reflection on medium $(i)$ of an incident wave. We show here that for any freely radiating body the existence of the *notion of emissivity* is in fact due to the presence of the interface, that is to say the discontinuity of a refractive index.

#### *2. Thermal radiation emitted by a substrate+film system*

The total emissivity of the *substrate+film* system used above Sec. II A is the sum of two contributions, which are independent because the waves concerned are incoherent with one another:

(a) the energy emitted by the substrate (medium 3) at the temperature $T$, seen through a deposited film (medium 2) which would have no thermal emission but would get the $\hat{n}_2$ index of the medium for this temperature,

(b) the energy emitted at the temperature $T$ by the film deposited on a substrate which would have no thermal emission but would get the $\hat{n}_3$ index for this temperature.

Substrate contribution: The waves emitted by $dV$ in medium 3 leave the system after multiple-transmissions and reflections in the film (with thickness $h$, Fig. 7). We assume that this film has no thermal emission but the value of $\hat{n}_2$ is the one for temperature $T$. With $|E_{3p}^t|^2=|E_{3s}^t|^2$ for $\theta=0$, then we calculate [Eq. (9)] the waves emitted in medium 1 by an element of volume at the depth $l$ as

$$E_3^t=I_3e^{i\omega t}t_{(2)/1}t_{(3)/1}e^{-i(2\pi/\lambda)\hat{n}_3 l}\times\left\{\sum_{j=0}^{+\infty}r^j_{(2)/1}r^j_{(2)/3}e^{-i(2\pi/\lambda)[\hat{n}_2(2j-1)h]}\right\}. \tag{20}$$

Hence, with $|E_3^t|^2=E_3^tE_3^{t*}$, the total energy due to medium 3 and emitted in medium 1 will be proportional to

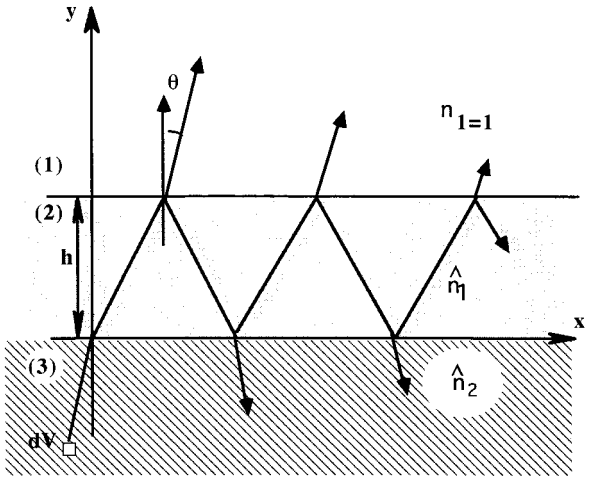


FIG. 7. Multiple reflection (in medium 2) of waves emitted by a volume $dV$ in medium 3.

$$W_{3/(2)/1}=\int_{-\infty}^{0}|E_3^t(y)|^2dy=\frac{I_3^2\lambda}{4\pi k_3}\left(\frac{|t_{(2)/1}t_{(3)/2}|^2}{Q(h)}\right)e^{-(4\pi/\lambda)k_2h}, \tag{21}$$

with $Q(h)$ a constant depending of $n_1$, $n_2$, $n_3$, $k_2$, $k_3$, $\lambda$, and depending on $h$, the thickness of the film.

As above [Eqs. (10), (18), and (19)] we can calculate the equivalent of an emissivity. This is the contribution of a substrate but seen through a film, and we can calculate a partial emissivity as follows:

$$\varepsilon_{3(2)1}=\left\langle\frac{S_{3/(2)/1}}{S_3}\right\rangle=\mathrm{Re}\left\{\frac{\hat{n}_1}{\hat{n}_3}\right\}\frac{4\pi k_3}{\lambda I_3^2}\,W_{3/(2)/1}, \tag{22}$$

with $S_3$ calculated from Eq. (10). When $h\to 0$, we check that $\varepsilon_{3(2)1}$ [Eq. (22)] is equal to $\varepsilon_{31}$ [Eq. (19)].

Film contribution: Similarly the element of volume $dV$ is now in medium 2. Here, two waves emitted from $dV$ can

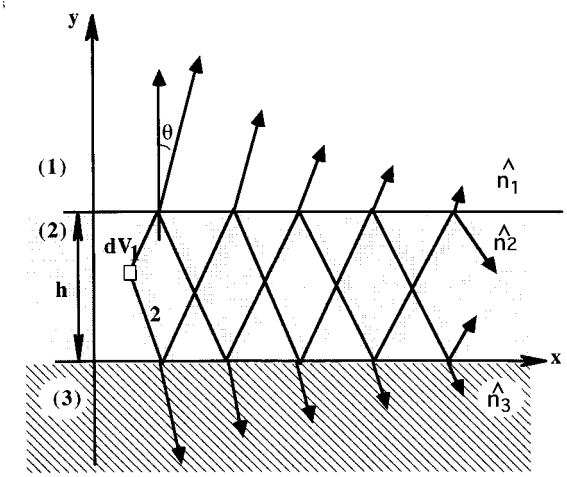


FIG. 8. Multiple reflection in medium 2 of waves emitted by a volume $dV$ of the film. Here waves 1 and 2 leave the film-substrate system under the same angle $\theta$.

emerge in the vacuum (Fig. 8). Waves 1 and 2 give, after multiple reflections and transmissions, emitted waves for which the energy is $|E_2^{1t}+E_2^{2t}|^2$ for $\theta=0$ and for wave 1:

$$E_2^{1t}=I_2 e^{i\omega t} t_{(2)/1} e^{-i(2\pi/\lambda)\hat{n}_2(h-l)} \times\left[\sum_{j=0}^{+\infty} r_{(2)/1}^{j} r_{(2)/3}^{j} e^{-i(2\pi/\lambda)\hat{n}_2 2jh}\right], \tag{23}$$

and for wave 2:

$$E_2^{2t}=I_2 e^{i\omega t} t_{(2)/1} r_{(2)/3} e^{-i(2\pi/\lambda)\hat{n}_2(h-l)} \times\left[\sum_{j=0}^{+\infty} r_{(2)/1}^{j} r_{(2)/3}^{j} e^{-i(2\pi/\lambda)\hat{n}_2 2jh}\right]. \tag{24}$$

For the whole thickness of the film the energy will be proportional to (integrating for $0<l<h$)

$$W_{21/(3)}=\int_{-\infty}^{0} |E_2^{1t}(y)+E_2^{2t}(y)|^2 dy. \tag{25}$$

The partial emissivity of this film deposited on a substrate which would have no thermal emission will be calculated as above [Eq. (22)], i.e.,

$$\varepsilon_{21(3)}=\left\langle \frac{S_{21/(3)}}{S_2}\right\rangle = \mathrm{Re}\left\{\frac{\hat{n}_1}{\hat{n}_2}\right\} \frac{4\pi k_2}{\lambda I_2^2} W_{21/(3)}, \tag{26}$$

with $S_2$, the Poynting vector of these waves emitted in medium 2 and calculated with the intensity $W_2$ as in Eq. (10). When $h\to+\infty$, we check that the result (26) is equal to $\varepsilon_{21}$, i.e.,

$$\varepsilon_{21(3)} \underset{h\to+\infty}{=} \varepsilon_{21}=\frac{4n_2}{(n_2+1)^2+k_2^2}. \tag{27}$$

As in Eq. (19), this partial emissivity is the real emissivity of a semi-infinite medium 2 emitting in vacuum.

Emissivity of the *substrate+film* system: The energetic contributions (with respect to the energy of waves emitted by a black body) for the film and substrate components have been calculated as partial emissivities. The proportion of energy (with respect to the black body) of the waves emitted by the system will be equal to the sum of these partial emissivities [Eqs. (22) and (26)], i.e.,

$$\varepsilon(h)=\underbrace{\mathrm{Re}\left\{\frac{\hat{n}_1}{\hat{n}_2}\right\} \frac{4\pi k_2}{\lambda I_2^2} W_{21/(3)}}_{\text{film}}+\underbrace{\mathrm{Re}\left\{\frac{\hat{n}_1}{\hat{n}_3}\right\} \frac{4\pi k_3}{\lambda I_3^2} W_{3/(2)/1}}_{\text{Substrate}}. \tag{28}$$

When the thickness of film $h\to+\infty$, we check that the second term of Eq. (28) tends to zero (substrate contribution) and the first one tends to $\varepsilon_{21}$ [Eq. (27)]. The energy of waves emitted by the substrate and transmitted through the film becomes negligible and the partial emissivity of the film becomes equal to the real emissivity ($\varepsilon_{21}$) of a half space of medium 2.

When, on the contrary, the thickness of the film tends to zero, the first term also tends to zero and the second term to $\varepsilon_{3(2)1}$, which is more complicated because of the presence of the reflection and transmission coefficients function of $n_2$ and $k_2$ which becomes equal to $\varepsilon_{31}$, i.e., the real emissivity of a half space of medium 3:

$$\varepsilon_{21(3)} \underset{h\to+\infty}{=} \varepsilon_{31}=\frac{4n_3}{(n_3+1)^2+k_3^2}. \tag{29}$$

By superposition, we check that the result of Eq. (28) is exactly similar to the final results obtained by using the previous indirect model, but this argument presents the problem of being based on the radiative phenomena really studied.

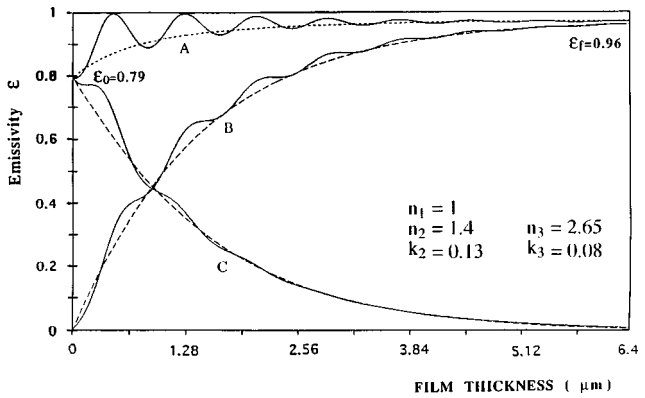


FIG. 9. Theoretical emissivity evolution $\varepsilon(h)$ during the growth of a deposit (medium 2, thickness $h$, refractive index $\hat{n}_2$) on an opaque substrate (medium 3, $\hat{n}_3$). $\varepsilon(h)$ is calculated by a usual direct model based on the McMahon method (dotted line) and by the direct model based on division of amplitude method (solid line). The curves noted *C* and *B* are, respectively, the partial emissivity evolutions of the deposited film and of the substrate under the deposit. The curves noted *A* are the global emissivity evolutions for the film-substrate system. The solid line *A* is exactly identical to the results of an indirect model based on thin film reflection theory calculated with concerned values of $\hat{n}_2$ and $\hat{n}_3$.

In Fig. 9 are plotted the numerical results of emissivity obtained by the three exposed models for the same values of $\lambda$, $\hat{n}_1$, $\hat{n}_2$, and $\hat{n}_3$, versus the thickness of a film (medium 2) deposited on substrate (medium 3). The values $n_2=1.45$, $k_2=0.13$, $n_3=2.65$, and $k_3=0.08$ are determined for the case of a diamond deposit on silicon substrate at 800 °C observed at $\lambda=2.3\ \mu$m. In dotted line are plotted the numerical results of the classical direct model [Eq. (4)] for the partial emissivity of the film and of the substrate seen through the film. The global result of the *film+substrate* system is represented by the dotted curve *A*. As mentioned above, this emissivity is monotonic and increasing steadily from $\varepsilon_0=0.79$, i.e., the substrate emissivity $\varepsilon_{31}$ [Eq. (29)] to $\varepsilon_f=0.96$, the final emissivity when the film is sufficiently thick to be considered as opaque [$\varepsilon_f=\varepsilon_{21}$, Eq. (27)]. The curves in solid line represent the numerical results of the direct model presented in this paper [Eq. (28)] for the partial emissivity of the film (curve *B*) and for the substrate (curve *C*). The evolution of the global emissivity of the *film+substrate* system [Eq. (28)] is presented by curve *A* (solid line) and is perfectly similar to the one obtained by the classical indirect model exposed Sec. II B [Eq. (5)].

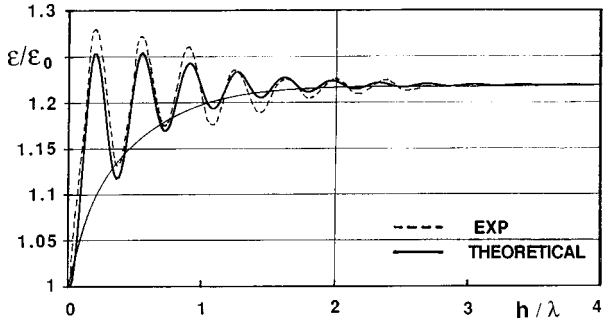


FIG. 10. Relative emissivity variations $\varepsilon/\varepsilon_0$ at $\lambda=2.3$ $\mu$m during growth of diamond on silicon substrate, vs the ratio $h/\lambda$ (dotted line). The treatment is performed at $T=800$ °C. These data are compared to the results of the interferential direct model (full thick line) and the results of McMahon-type model (full thin line). These theoretical results have been obtained using layer by layer growth assumption from the beginning of the reaction, and with $n_2=1.45$, $k_2=0.13$, and $n_3=2.65$, $k_3=0.08$.

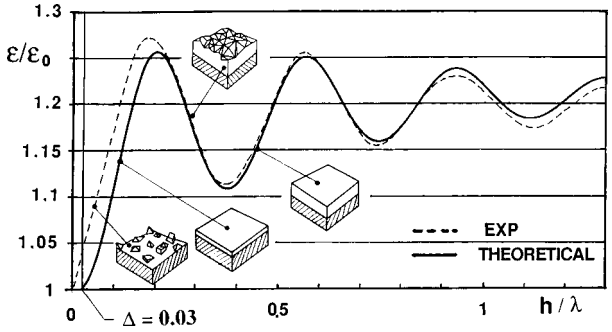


FIG. 11. Relative emissivity variations $\varepsilon/\varepsilon_0$ at $\lambda=2.3$ $\mu$m during the first stage of diamond film growth on silicon substrate, performed at $T=850$ °C (dotted line). The number of initial growth sites has been measured equal to $\sim 2\times 10^8$ cm$^{-2}$. The solid line shows the results of the interferential direct model based on a layer by layer growth of the deposited film, but with an initial offset $\Delta$ and for $n_2=1.45$, $k_2=0.13$, and $n_3=2.65$, $k_3=0.08$.

## III. EXAMPLE OF APPLICATION

The growth of thin diamond layers on a silicon substrate was studied by pyrometric observations. The deposit was obtained by a microwave-plasma-assisted CVD. The pyrometric observations were carried out at a wavelength of 2.3 $\mu$m with an Ircon 6-15C15 pyrometer from the early stage of the treatment. During the experiment the temperature was controlled by a thermocouple.[23,29]

Pyrometric signal oscillations are observed during the initial stage of the growth of the film [Fig. 1(d)]. In spite of the variation of the apparent temperature, the actual temperature of the sample remains constant during the reaction. These oscillations are due to the emissivity variations, easy to obtain from the pyrometer signal. They cannot be predicted by usual direct theory [Fig. 1(d)].

Figure 10 shows these experimental emissivity variations $\varepsilon/\varepsilon_0$ vs the ratio $h/\lambda$, during diamond deposition on silicon substrate at a temperature equal to 800 °C.[23] $h$ is the film thickness at time $t$, $\lambda$ the wavelength observed by the pyrometer and, $\varepsilon/\varepsilon_0$ the ratio of emissivity at time $t$ on the emissivity before treatment, i.e., in this case silicon emissivity. Thickness $h(t)$ is obtained by the measurement of the total thickness at the end of the treatment (by scanning electron microscopy) and assuming a linear kinetic law $h(t)=kt$.

In this figure we note that the emissivity variations take place in the range where McMahon's model (dotted line Fig. 10) is irrelevant. Indeed, the film thickness is here smaller than or in the same order as $\lambda$ $(0<h<2\lambda)$, and largely inferior to the coherence length $\lambda^2/\Delta\lambda$ of the observed radiations.

On the contrary, we can see that the direct model presented here (full line, Fig. 10) can describe quite closely the experimental observations. By adjustment of the theoretical parameters to fit the experimental behavior, we can determine several characteristics of the material during deposition. For instance, we obtained here the previously unknown index of diamond $\hat{n}_2$ at 800 °C.[23]

Nevertheless, in some cases there is a small range of growth, at the very beginning, where the data are not very well fitted. Actually, during the first stage of the reaction, the optical calculation based on the layer by layer growth [two-dimensional (2D) homogeneous] is not relevant when the number of nucleation sites is too small. This was observed for diamond film growth[30] as well as for the first stage of oxide layer growth on metal.[5]

In Fig. 11, we can see the emissivity ratio $\varepsilon/\varepsilon_0$ at $\lambda=2.3$ $\mu$m vs ratio $h/\lambda$, observed[31] during a diamond growth performed at 850 °C on a different silicon substrate with a nucleation density inferior to 2 $10^8$ cm$^{-2}$. We verify that our direct model based on a layer by layer growth is well adapted for $h/\lambda>0.3$, with a delay ($\Delta$) applied at the beginning of the numerical curve. In fact, we know by scanning electron microscopy observations[30] that the growth begins by a nucleation stage, which explains the previous delay.[31] The crystallites are then very small and randomly distributed. Only after $h/\lambda\approx 0.3$, these crystallites are joined and cover the whole surface. Today we can describe the evolution of this heterostructure versus time.[32,33] Thus we know that the layer by layer model is correct by first approximation from the time of crystallite coalescence. From this coalescence threshold, apart from the residual microroughness,[34,35] the radiating sample can be considered as a 2D homogeneous system and can show the optical behavior of a thin compact film deposited on a substrate. Then the fitting becomes quite accurate [Fig. (11)].

Under the coalescence threshold, it would be necessary to calculate the emissivity of a randomly mesoscale heterostructure. Similarly it would be necessary to take into account the influence of the residual roughness on the compact film. For this kind of structure, $\rho$, $\tau$, and $\alpha$ are calculated when possible by using the effective medium theories, for instance for diamond.[25] We should note that this is another case where Kirchhoff's law in the usual indirect argument is far from being automatically applicable. Therefore, the direct argument described in this paper opens the way to new perspectives in studying the radiative power of mesoscale structures such as, for example, composite materials, granular or porous films, and so on.

## IV. CONCLUSION

In this paper, we showed that a direct method based on the division of amplitude can be used to calculate directly the

emissivity of a *substrate+film* system, without using Kirchhoff's second law. This method consists in considering an inhomogeneous material on the scale of the radiation concerned; for example, the thickness of a thin film on a massive opaque substrate, as a juxtaposition of Planckian sources, emitting incoherent waves.

We checked that the classical direct models such as McMahon's based on the simple addition of the energies of waves emitted by each volume element, do not allow us to describe the real behavior experimentally recorded in this scale range. We showed here that they are actually only appropriate for calculating the emissive power of thick films, where the thickness($h$) is larger than the coherence lengths of the observed radiation in the range $\lambda \pm \Delta\lambda/2$.

On the other hand, the application of this direct model of thermal emission for a material system with mesoscopical structure—for example for a film whose thickness is inferior to or of the same order as the wavelength—shows that it is actually possible to describe the emissivity fluctuations experimentally observed. It describes these fluctuations exactly as predicted by the indirect model using Kirchhoff's second law. As a matter of fact we note the similarity, especially in the case studied here, of deposited thin films, between the results of the model proposed and those obtained by the indirect argument. In return, it confirms the supposed validity of Kirchhoff's relation in this particular case. However, different problems arise for the user of the indirect argument: the effective medium needed for the indirect resolution does not always exist; one instance is in the vicinity of a percolation threshold for optical phenomena. Besides, the use of Kirchhoff's second law to calculate the emissivity of mesoscopical materials with complex structure is far from clear. In fact, most of the time, this argument by default concerning *inhomogeneous* materials uses, at the end of the calculation, Kirchhoff's law which implicitly assumes a *homogeneous* system without any justification.

This direct model concerns the thermal emission phenomenon actually studied. In particular, it allows one to point out interferential phenomena in emissivity, which is usually considered an incoherent and diffuse phenomenon. Therefore, this direct model is, from a theoretical point of view, an interesting alternative for the calculation of the emissive properties of a complex mesoscopical structure. For example, this direct model can be easily extended to the calculation of multilayer materials. The case given in this paper of the *in situ* study of the growth of diamond film on silicon seems promising in this way. It also shows the possibilities offered by this approach for the diagnosis and control, *in situ* and in real time, of surface reactions and growth processes.


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