Modelling of Deposition of Small Particles from the Vapour State on a Thin Film

Rahul Basu

Emeritus Professor, JNTU

Hyderabad, Telengana, raulbasu@gmail.com

Abstract.

The Technology of film deposition onto a substrate has found use in many areas, including coatings for stealth applications, diamond film coatings, and tool coatings for hardness. A model is developed for the direct transformation from the vapour state to solid state, and related to the boundary conditions and other material parameters. Spherical particle Morphology is used for the modeling. Apart from a theoretical formulation and solution, a numerical approach with a graphical solution using computational tools is attempted. The effect of various boundary conditions and material parameters is found by numerical simulation. The results can be used in effective film deposition by tuning of parameters.

Keywords. ***–Sublimation, eigenvalues, diffusion, moving boundary problem, thin film***

1. INTRODUCTION

Very few substances are known to sublimate directly to vapur without passing through the liquid phase. Among these are Iodine, carbon, naphthalene, dry ice and a few others. The reverse process known as deposition occurs in, for example, water vapour to ice in the form of frost. In the following it is attempted to illustrate the deposition of diamond from vapour for varying imposed conditions.

The production of diamond films and crystals from vapour by various reduction reactions has recently been applied to industrial application. Diamond film has interesting physical and chemical properties. The properties relating to sublimation were catalogued Hoch etal [1], by pressure measurement methods. Production of artificial diamonds was perhaps the earliest motive for technology development, yet the costs were prohibitive. More recently, diamond coatings and films were developed and have industrial use [2,3]. Some of the methods include CVD and plasma assisted CVD, [4]. A 2D model for the CVD of SiN was proposed by Evans [5]

2. MATHEMATICAL MODEL

The diffusion equations for thermal and mass transport in spherical coordinates can be transformed by a simple change of variable to one dimension. By U=rT

Where $K \nabla^2 T = \rho c_p \, dT/dt$ (1)

$K(1/r^2 \, d/dr(r \, dT/dr)) = \rho c_p \, dT/dt$ (2)

$K/r^2[d/dr(r^2 \, dT/dr)] = K/r \, d^2U/dr^2 = \rho c_p \, d(U/r)/dt$

$= \rho c_p \, /r \, (dU/dt)$ (3)

So $K \, d^2U/dr^2 = \rho c_p \, (dU/dt)$, whence using similarity variable $\eta = r/(\alpha t)^{1/2}$ (4)

$U'' + \eta/2 \, U' = 0$ (5)

similarly for mass transfer.

Applying the transformation $U' = p$

$p' = -\eta/2 \, p$, which is easily solved. (6)

One solution is $(\ln p) = - \eta^2/4 + A$ (7)

$P = U' = A \exp(-\eta^2/4) d\eta + B$, whence (8)

$U = A \, erf (\eta/2) + B\eta$, $T = U/r$

Applying the energy balance across the phase interface,

$K \, d\Theta/d\eta = L\rho \, ds/dt$ (9)

Since $\eta = r/(at)$ ½

Using the chain rule, the result becomes

$K \, d(U/r)/d\eta = L\rho \, ds/dt$, after simplifications

$K \, d(U/r)/d\eta = L\rho \, \alpha \, \Lambda^2/2$ (10)

Further substitution and simplification gives the balance

$KA[\Lambda \exp(-\Lambda^2/4) - erf(\Lambda/2)] = \rho L \Lambda^3 \alpha/2$ (11)

where A is a constant depending on the B.C.

3.RESULTS

The properties for water ice as given in Paterson[5]

Water : $k_2 = 0{\cdot}00144$ Cal/cm. sec.° K. $K_2 = 0{\cdot}00144$ cm.²/sec.
Ice : $k_1 = 0{\cdot}0053$ Cal/cm. sec.° K. $K_1 = 0{\cdot}0155$ cm.²/sec.
and $L\rho$ (ice) $= 73{\cdot}6$ Cal/cm.³

For ice –vapour the value for $L\rho = 618$ Cal/cm^3

For the spherical geometry, well known solutions have been given for conduction by Carslaw Jaeger [6], and for phase melting by Paterson [7].

Using the solution from [7] for simplicity,

$$\frac{q}{4\pi} e^{-\alpha^2/4K_2} - \frac{k_1 \alpha \Theta}{1 - \frac{\alpha}{2}\sqrt{\frac{\pi}{K_1}}\, e^{\alpha^2/4K_1}\, \operatorname{erfc}\left(\frac{\alpha}{2\sqrt{K_1}}\right)} = \frac{L\rho\alpha^3}{2} \qquad (12)$$

q is a point source strength and Θ the initial temperature. Putting Q=0, and varying the initial temperature from -5 to 5, solutions for α are obtained as shown in Fig 1.

plot $\quad -0.0053 \times \dfrac{T}{1 - \frac{x}{2}\sqrt{\frac{\pi}{0.0155}}\, \exp\left(\frac{x^2}{4 \times 0.0155}\right) \operatorname{erfc}\left(0.5 \times \frac{x}{\sqrt{0.0155}}\right)} = 613.6 \times 0.5\, x^2 \quad T = -5 \text{ to } 5$

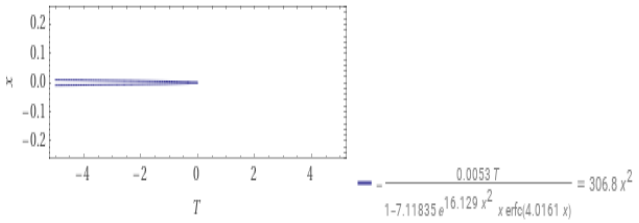


Fig. 1 Solutions for water vapour-ice From values in[7]

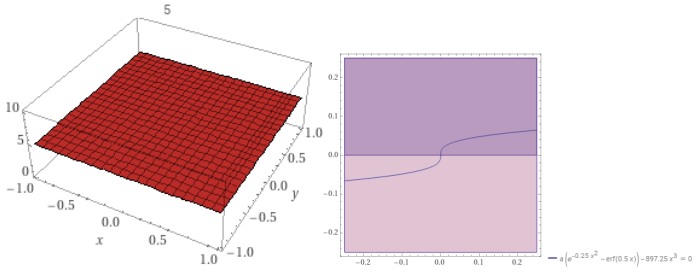


Fig 2. Implicit plot for ice

Using the solution obtained for U, for Diamond , if A=1

$$e^{-x^2/4}\,x - \operatorname{erf}\left(\frac{x}{2}\right) = 122\,485.\,x^3 \qquad (13)$$

Applying Wolfram similar graphs are obtained, eigenvalues as

A=1 Solution x ≈ -0.00188628634813420...

A=5 x ≈ -0.00421785051971876...

It can be seen that the rate changes with A, depending on the B.C. By WOLFRAM using plot function on the expression

| A (exp(-0.25 x x) - erf(0.5 x)) + x^3×(-122.485)

the form of solution varying with A is shown below:

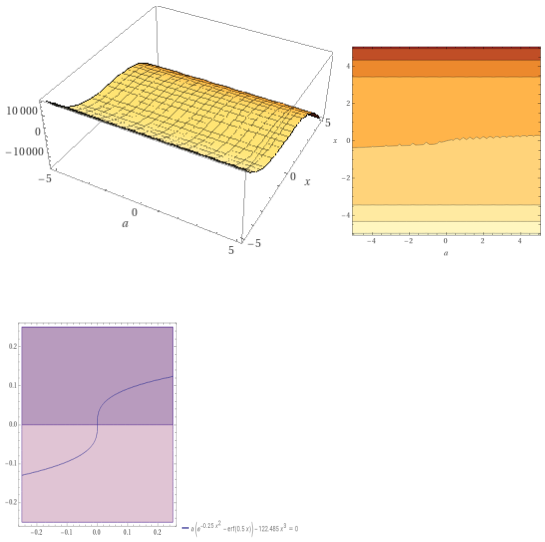


Fig.3. Contour and implicit plots of diamond for x vs A

Thus variations can be obtained by either adjusting the heat transfer rate or the initial temperatures. Using the formula in Paterson (5) with initial temperature as the variable, varing from -5 to 5, the results obtained are as:

manipulate

plot $(6a)\Big/\left(1-0.333772\,e^{0.035461\,x^2}\,x\,\operatorname{erfc}(0.188311\,x)\right)=104242\,x^2$ $x=a-5$ to 5

varying a

(14)

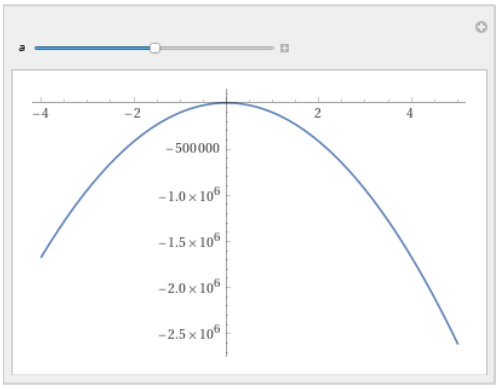


Fig 4. Solution of (14)

TABLE 1

Sublimation rate of Carbon vs initial temperature

Initial temperature	Sublimation value
5	-.0495
4	-.0441
3	-.0382
2	-.0311
1	-.022

As a benchmark value, take the eigenvalue as .01, then the radius over time given by $r= \Lambda(\alpha t)^{1/2} = .026t^{1/2}$

Using the formula based on heat transfer rate (13), the thickness over time is $.001t^{1/2}$

4. **Discussion and Conclusion**

By using the substitution developed for the spherical deposition in (11), it appears that the variation depends on the cubic power of the eigenvalue Λ. However the deposition rate for diamond is far less than that of ice. Similar results are obtained if the formula developed in [7] for initial temperature as the condition is used. The temperature of transformation at equilibrium is conventionally taken at the triple state, Chaoping [9]

The physical model for deposition of crystals like diamond can be presumed to start with spherical nuclei in the nano regions. Since facets of crystal grow with equal probability in all preferred directions, the spherical model is a reasonable mathematical assumption. Most commonly, the amorphous version of the deposit occurs. Since graphite is more stable than diamond, it is difficult to obtain the crystalline form of the element, .

The phase diagram below shows the various regions where diamond formation is possible, using pressure. It can be seen that the production of diamond requires pressure of 40 to 50 GPa and temperatures of 2000K to 3000K.

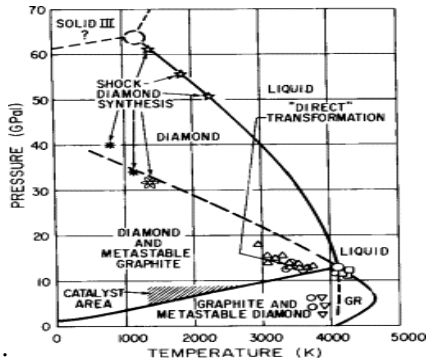


Fig.5 Pressure Temperature diagram for diamond

(from Wenthorf and devries [8])

Sublimation kinetics have also been evaluated for graphite and graphene by Long [10], where variation in surface properties of nano particles is stated to affect ensemble averaged estimates.

Due to the slow rates in direct deposition, other methods using reduction of carbon compound vapours and gases have been applied commercially. Apart from the initial attempts at high pressure and temperature, the expense involved for industrial production has made successful efforts a closely guarded area.

5.REFERENCES

[1] Hoch M, BPE, Dingledy DP etal, "The Heat of Sublimation of Carbon, *J Phys Chem*, 59, 2, 1955

[2] Ladwig A, Koch R, Wensky E, "Atmospheric Plasma Deposition of DLC coatings", *Diamond Related Materials, 18, 1129-1133, 2009*

[3] Roy, M. "Protective Hard Coatings for Tribological Applications. Materials Under Extreme Conditions"*, 259–292.* doi:10.1016/b978-0-12-801300-7.000,2017

[4] Ohring, M. "Chemical Vapor Deposition. Materials Science of Thin Films"*, 277–355.* doi:10.1016/b978-012524975-1/50009-4,2002

[5] Evans G, Greif R, "A two-dimensional model of the chemical vapour deposition of silicon nitride in a low-pressure hot-wall reactor including multi-component diffusion", *Int. J. Heat Mass Transfer*. Vol. 37. No. 10. pp. 1535-1543, 1994

[6] Carslaw HS Jaeger JC, *Conduction of Heat in Solids*, OUP, 1986

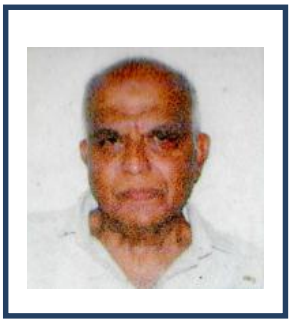
[7] Paterson S, "Propagation of a Boundary of Fusion*",GlasgowMathJnl*,1952,DOI:10.1017/S2040618500032937

[8] Wentorf, R. H., & DeVries, R. C. High-Pressure Synthesis (Chemistry). *Encyclopedia of Physical Science and Technology, 365–379.* doi:10.1016/b0-12-227410-5/00968-6 ,2003

[9] Chaoping M, Guangdon Z,Zhiwei Z, "A Modified S-L-G Phase equation of states", *ACS Omega* , 7, 9322-9332,2022

[10] Long B, Lau C, Rodriguez D etal, "Sublimation Kinetics for Individual Graphite and Graphene Nanoparticles (NPs): NP-to-NP Variations and Evolving Structure-Kinetics and Structure-Emissivity Relationships", *J. Am. Chem. Soc.*, 142, 33, 14090–14101, 2020

Biographies



Rahul Basu received the bachelor's degree in Mechanical engineering from the California Institute of Technology in 1970, the master's degree in Materials Science and engineering from the University of California, LA in 1973, and the doctorate degree in from Eurotechnical University in 1991, respectively. After working at the Indian Institute of Science, and DRDO on forming of super alloys and rotor dynamics, receiving three Indian Patents, he is currently an Emeritus Professor, UGC with JNTU and VTU Bangalore. His research areas include amorphous alloys, Nano composites and Renewable Energy. He has been serving as a reviewer for many highly-respected journals.