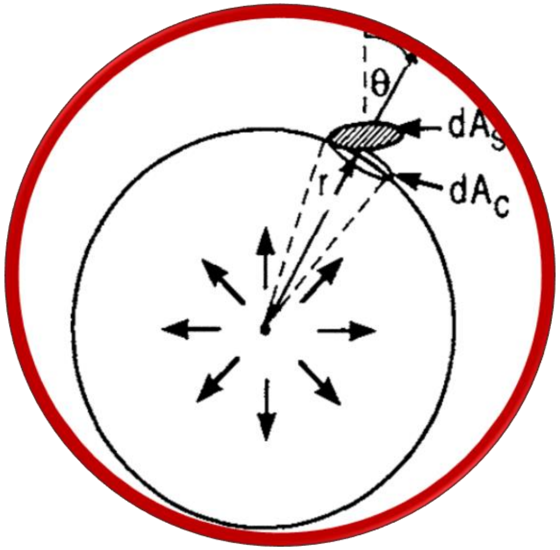
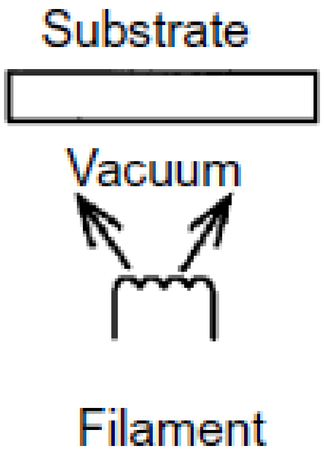
evaporation



contents

- Vapor pressure and evaporation rate
- Deposition geometry and film uniformity
- Step coverage
- Film purity
- Thermal evaporation
- Ebeam evaporation
- Pulsed laser evaporation
- Ion beam assisted evaporation
- Arc evaporation

evaporation

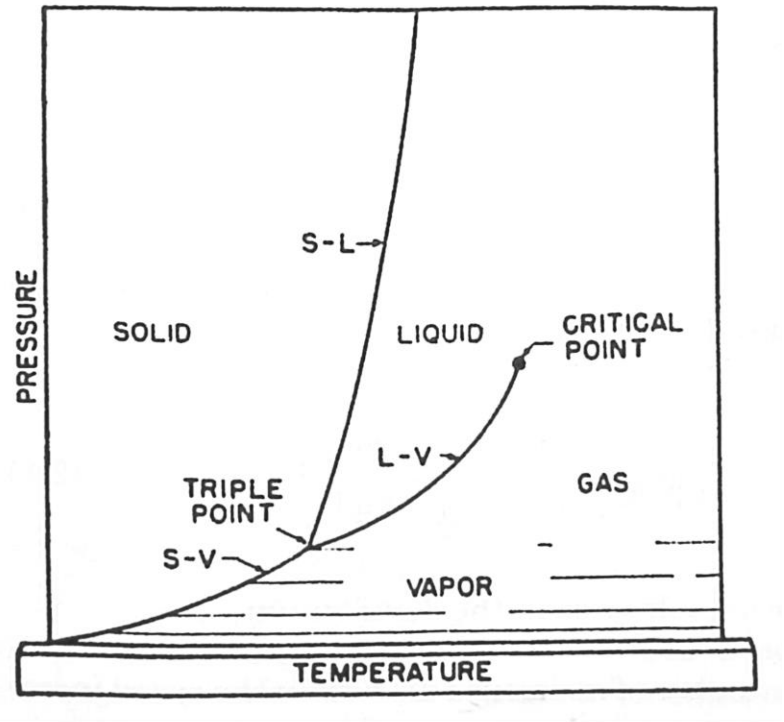


To which T should we heat?
How should we heat? Will the evaporant react with the crucible/wire?
Which vacuum level will be ideal?
Distribution of the deposit on the substate? How on a surface with topography?

Smith 1995

PT diagram

It is important to distinguish between the behaviors of vapors and gases.



Critical point: the volume difference between the liquid and the gas vanishes and there is no distinction between the two phases

Triple point: all three phases can exist simultaneously in equilibrium

Smith 1995

evaporation rate

It has been found experimentally that evaporation rates are proportional to the difference between the

equilibrium pressure, P_e ,

of the evaporated material at the given temperature and the

hydrostatic pressure, P_h,

acting on the evaporant. The basic equation for the rate of evaporation from both liquid and solid surfaces is

$$\phi_e = \alpha_e N_A \,(P_e - P_h)/\sqrt{2\pi MRT}$$

the evaporation flux ϕ_e in number of atoms (or molecules) per unit area, per unit time, and α_e is the coefficient of evaporation, which has a value between 0 and 1.

When α_e = 1 and P_h is zero, the maximum evaporation rate is realized and we obtain

$$\phi_e = 4.68\,10^{22} P_e/\sqrt{MT}$$

in molecules/cm^2 s and with P_e in mbar.

As a rule of thumb many evaporants show at 10^{-2} mbar a mass evaporant rate Γ_e of approx. 10^{-4} g/s cm^2

Ohring 2002

vapor pressure of elements

The Clausius-Clapeyron equation, describes both solid-vapor and liquid-vapor equilibria

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta H(T)}{T\Delta V}$$

As a first approximation, $\Delta H(T)$ = ΔH_e, the molar heat of evaporation (a constant), and $\Delta V \approx \Delta V_e$= RT/P in which case simple integration yields

$$\ln P = \frac{\Delta H_e}{RT} + I \qquad \text{or} \qquad P = P_0\, \mathrm{e}\,x\,\mathrm{p} - \frac{\Delta H_e}{RT}$$

where I (or P_0 = exp I) is the constant of integration.

For practical purposes adequately describes the temperature dependence of the vapor pressure in many materials.

Practically through substitution of the latent heat of vaporization ΔH_V for ΔH_e the boiling point for T, and 1 atm for P, the value of I can be determined for the liquid-vapor transformation.

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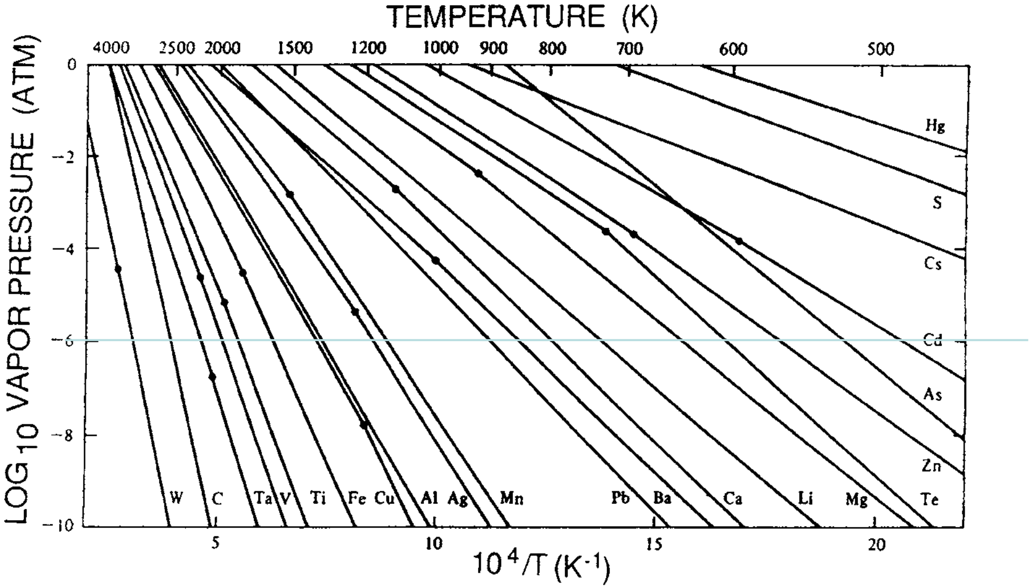
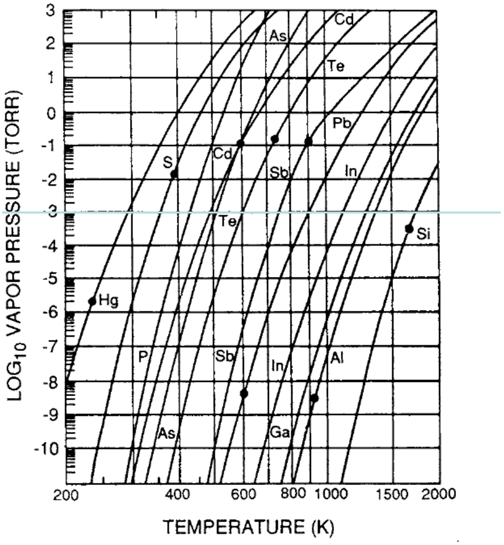
vapor pressure of elements





Dots correspond to melting points. Two modes of evaporation can be distinguished in practice depending on whether the vapor effectively emanates from a liquid or solid source.

As a rule of thumb, a **melt will be required if the element in question does not achieve a vapor pressure greater than 10^{-3} mbar at its melting point**.

Some metals fall into this category and effective film deposition by evaporation is attained only when the source is molten.

On the other hand, **elements such as Ti, Fe, and Si reach sufficiently high vapor pressures below the melting point and, therefore, sublime**.

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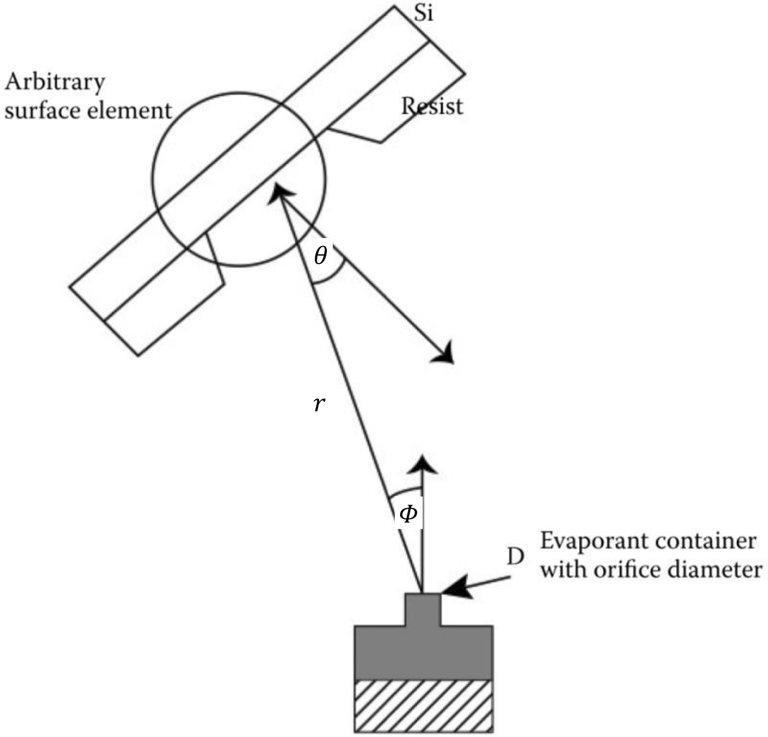
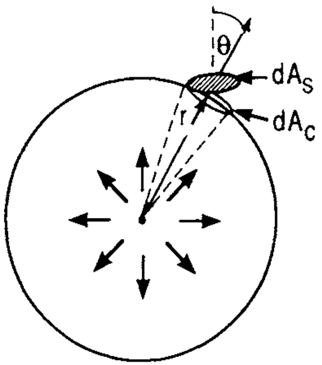
deposition geometry



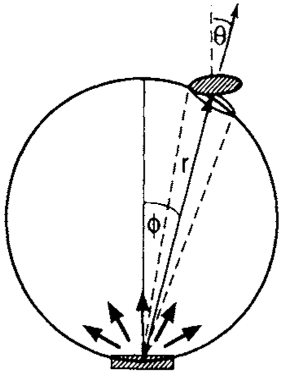
$$deposition\ rate \sim \frac{\cos\Phi \cos\theta}{r^2}$$

Madou 2012

deposition geometry



POINT SOURCE



SURFACE SOURCE

If we can treat the source **as point source** then the total evaporated mass M_e is then given by the double integral

$$M_e = \int_0^t \int_{A_c} \Gamma_e \, \mathrm{d}A_e \, \mathrm{d}t$$

Of this amount, mass dM_s falls on the substrate of area dA_s. Since the projected area dA_s on the surface of the sphere is dA_c, with $dA_c = dA_s \cos\theta$, the proportionality holds that $dM_s : M_e = dA_C : 4\pi r^2$

Finally we obtain

$$\frac{\mathrm{d}M_s}{\mathrm{d}A_s} = \frac{M_e \cos\theta}{4\pi r^2}$$

on a per-unit time basis we speak of the film deposition rate/~ (atoms/cm^{2}s), a term that has the same units.

The deposition varies **with the geometric orientation of the substrate** and **with the inverse square of the source-substrate distance**! Substrates placed tangent to the surface of the receiving sphere would be coated uniformly irrespective of placement since $\theta = 0$ and $\cos\theta = 1$.

For a **surface source** we would obtain

$$\frac{\mathrm{d}M_s}{\mathrm{d}A_s} = \frac{M_e cos\Phi \cos\theta}{\pi r^2}$$

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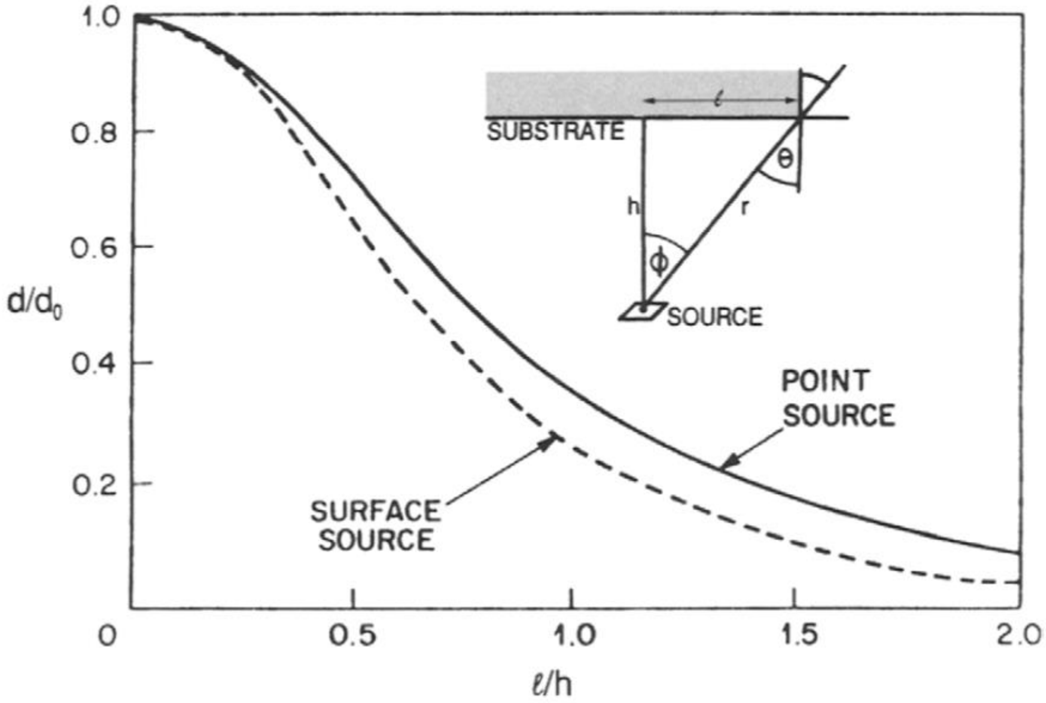
film thickness uniformity



Example for film thickness uniformity for point and surface sources.
Less thickness uniformity can be expected with the surface source.

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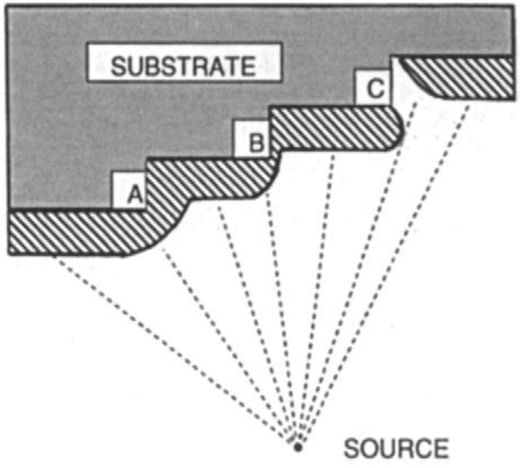
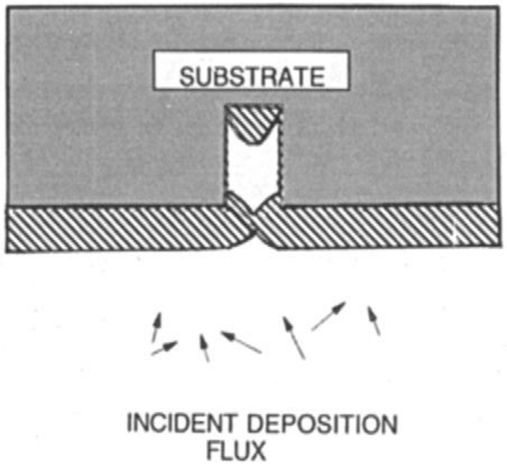
conformal coverage of steps and trenches





Schematic illustration of film coverage of stepped substrate.

A: Uniform coverage;
B: poor sidewall coverage;
C: lack of coverage--discontinuous film.

Bottom: Formation of a keyhole void in a high aspect ratio via during sputtering

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film purity

The chemical purity of evaporated films is dependent on the nature and level of impurities that

(1) are **initially present in the source**,
(2) contaminate the source from the **heater, crucible, or support materials**, and
(3) originate from the **residual gases** present in the vacuum system.

During deposition both the evaporant and residual gases impinge on the substrate. Dimensional analysis shows that the evaporant vapor impingement rate is $\rho N_A \dot{d}/M_a$, where ρ is the film density and $\dot{d}$ is the deposition rate (cm/s).

Simultaneously gas impinges as derived earlier and we obtain the ratio of the latter to former impingement rate is the gas impurity concentration C_i

$$C_i = \frac{7.76 \times 10^{-2} P M_a}{\sqrt{M_g T} \rho \dot{d}}$$

Terms M_a and M_g refer to evaporant and gas molecular weights, respectively, and P is the residual gas vapor pressure in mbar.

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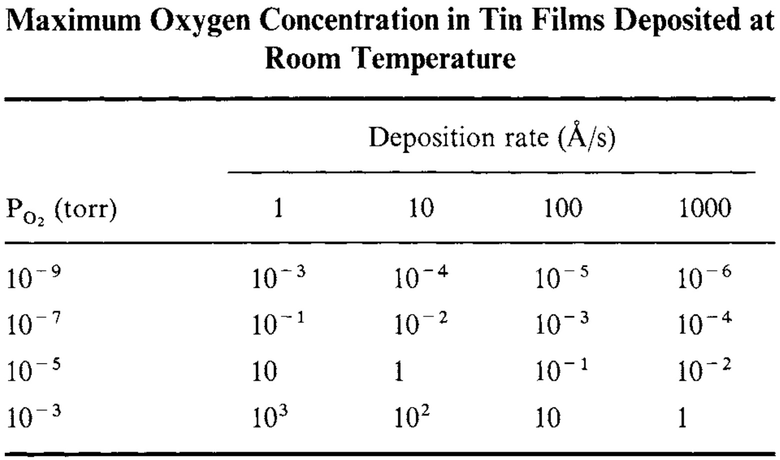
film purity



Maximum Oxygen Concentration in Tin Films Deposited at Room Temperature

	Deposition rate (Å/s)			
P_{O_2} (torr)	1	10	100	1000
10^{-9}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
10^{-7}	10^{-1}	10^{-2}	10^{-3}	10^{-4}
10^{-5}	10	1	10^{-1}	10^{-2}
10^{-3}	10^{3}	10^{2}	10	1

The table for C_i illustrates the combined role that deposition rate and residual gas pressure play in determining the oxygen level that can be incorporated into tin films. Although the concentrations are probably overestimated because the sticking probability of O_2 is of the order of 0.1 or less, the results have several important implications.

In order **to produce very pure films**, it is important to

(1) deposit at very high rates

(2) while maintaining **very low background pressures of residual gases** such as H_2O , CO_2, CO, O_2, and N_2.

Neither of these requirements is too formidable for vacuum evaporation where deposition rates from electron beam sources can reach 100 nm/s at chamber pressures of ~ 10^{-8} mbar.

.

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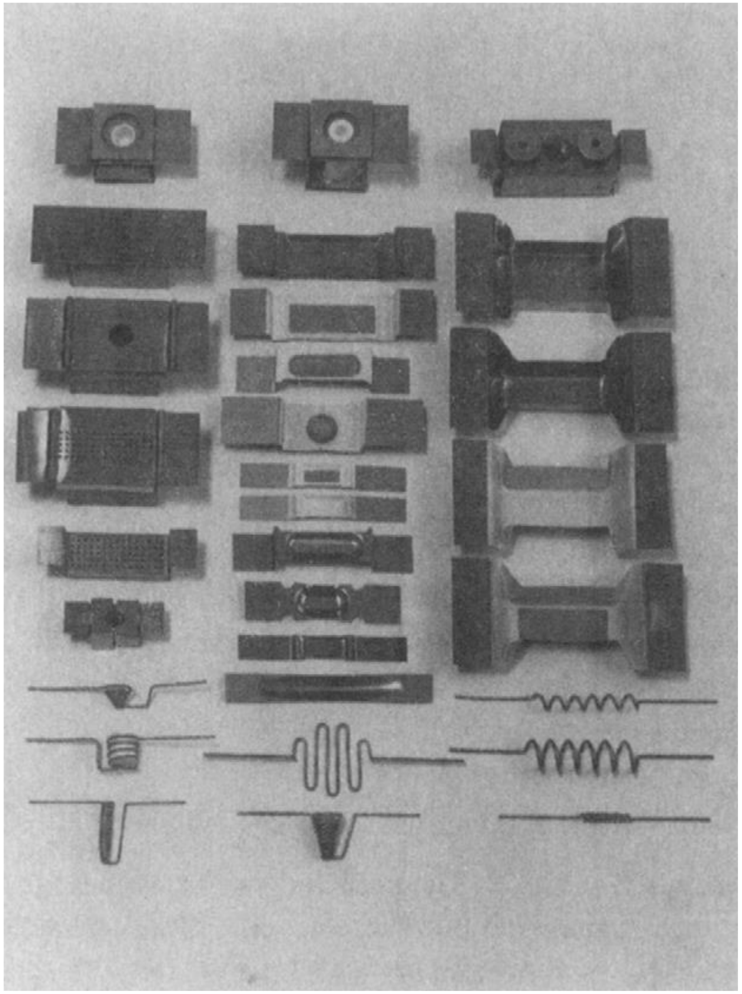
evaporation hardware I



Tungsten wire sources
Refractory metal sheet sources
Sublimation sources
Crucible sources

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application of thermal evaporation

- Electrically conductive coatings – ceramic metallization (e.g. Ti–Au, Ti–Pd–Au, Al, Al–Cu–Si, Cr–Au, Ti–Ag), semiconductor metallization (e.g. Al : Cu (2%) on silicon), metallization of capacitor foils (e.g. Zn, Al).
- Optical coatings – reflective and AR multilayer coatings, heat mirrors, abrasion resistant topcoats
- Decorative coatings (e.g. Al, Au on plastics).
- Moisture and oxygen permeation barriers – packaging materials (e.g. Al and SiOx on polymer webs).
- Corrosion-resistant coatings (e.g. Al on steel).
- Insulating layers for microelectronics.
- Selenium coatings for electrography or xerography.
- Vacuum plating of high strength steels to avoid the hydrogen embrittlement associated with electroplating (e.g. Cd on steel – "vacuum cad plating").

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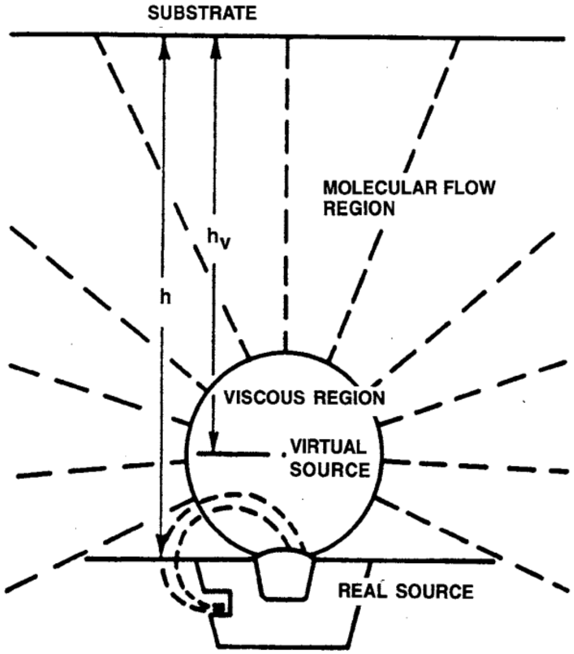
evaporation hardware II – ebeam evaporators

Disadvantages of resistively heated evaporation sources include contamination by crucibles, heaters, and support materials. This makes it difficult to deposit pure films or evaporate high-melting-point materials at appreciable rates.

Electronbeam (e-beam) heating eliminates these disadvantages and has, therefore, become the preferred vacuum evaporation technique for depositing films.



electrons are thermionically emitted from **heated filaments** that are **shielded from direct line of sight** of both the evaporant charge and substrate.

Film contamination from the heated cathode filament is eliminated this way.

The cathode potential is biased negatively with respect to a nearby grounded anode by anywhere from **4 to 20 kilovolts, and this serves to accelerate the electrons.**

In addition, a **transverse magnetic field is applied that serves to deflect the electron beam in a 270° circular arc** and focus it on the hearth and evaporant charge at ground potential.

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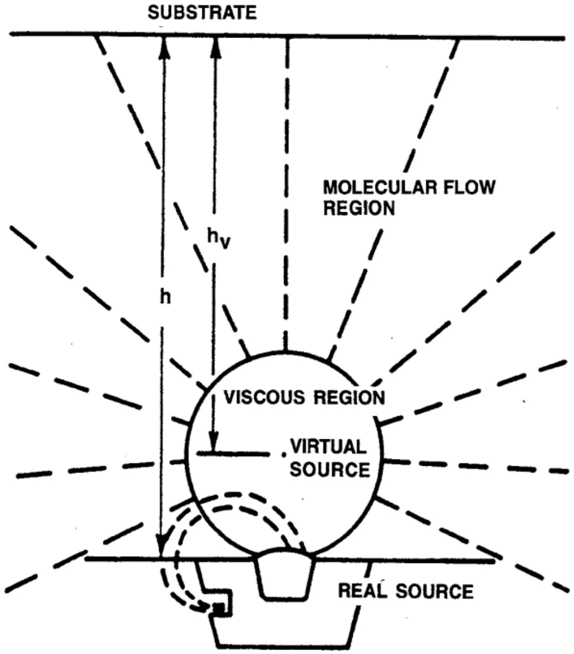
evaporation hardware II – ebeam evaporators



At the higher evaporation rates, including those usually employed in practice, the vapor just above the hearth approximates a high-pressure viscous cloud of very hot evaporant.

The region beyond this dense cloud is at much lower pressure and so we may assume molecular flow prevails.

Thus, instead of evaporant particles being beamed from various points on the flat source surface, they appear to originate from the perimeter of the viscous cloud.

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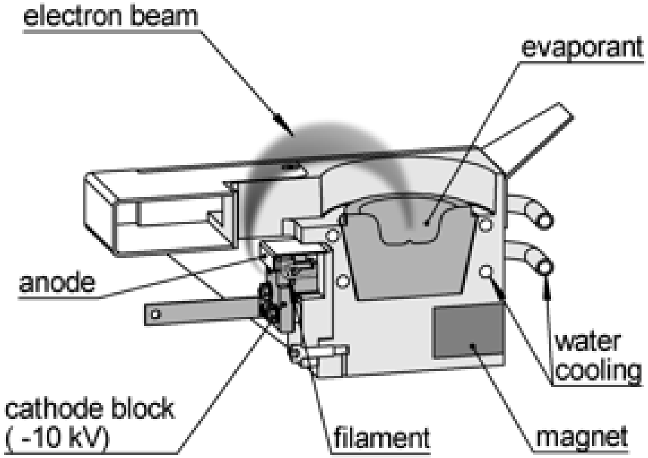
evaporation hardware II - ebeam evaporators



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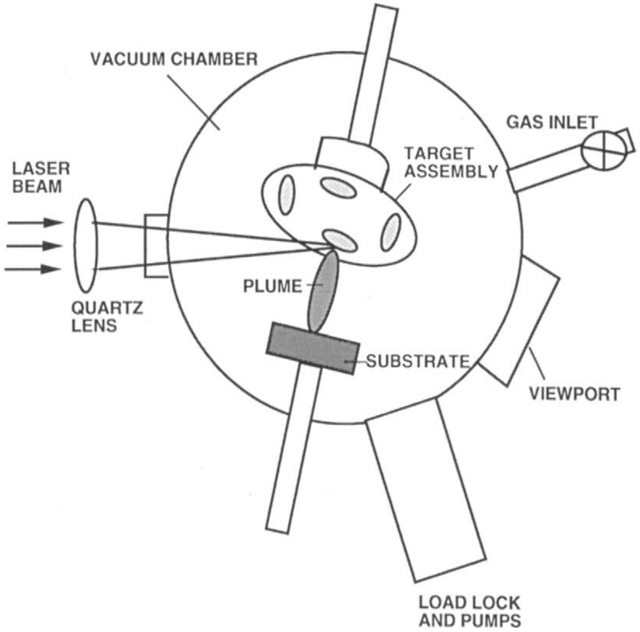
https://www.mbe-komponenten.de/products/mbe-components/e-beam-evaporators/ebv.php

evaporation hardware III – pulsed laser deposition



In its simplest configuration, **a high-power laser situated outside the vacuum deposition chamber** is focused by means of external lenses onto the target surface, which serves as the evaporation source.

Most **nonmetallic materials that are evaporated exhibit strong absorption in the ultraviolet spectral range between 200 and 400 nm**. Absorption coefficients tend to increase at the shorter wavelengths meaning reduced penetration depths.

Irrespective of laser used, the absorbed beam energy is converted into thermal, chemical, and mechanical energy, causing **electronic excitation of target atoms, ablation** and **exfoliation of the surface**, and **plasma formation**.

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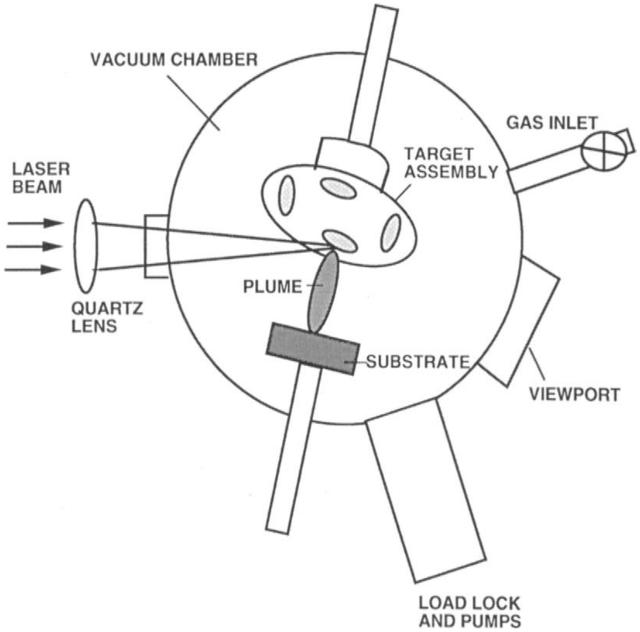
evaporation hardware III – pulsed laser deposition



Evaporants form a plume above the target consisting of a collection of energetic neutral atoms, molecules, ions, electrons, atom clusters, micronsized particulates, and molten droplets and its contents are propelled to the substrate where they condense and form a film.

Gases, e.g., O_2, N_2, are often introduced in the deposition chamber to promote surface reactions or maintain film stoichiometry.

PLD is in particular capable of deposition of **stoichiometric ceramic films**, which is not easily achieved by other means.

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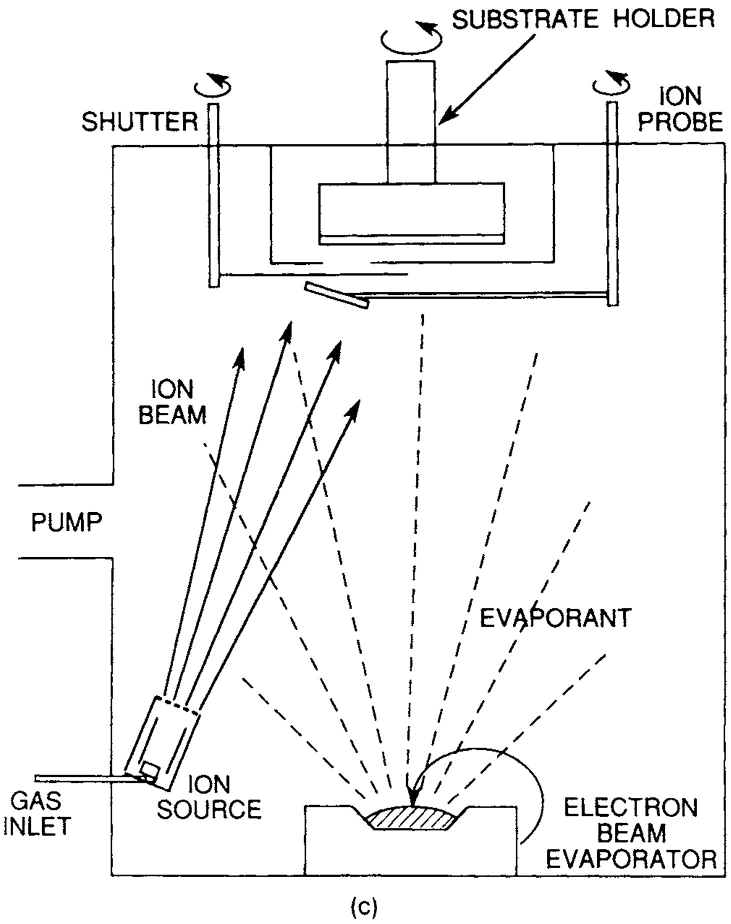
evaporation hardware III – pulsed laser deposition

Markets	Application	Materials
OLEDs and LEDs	Anti Reflection, TCOs, barriers	Al_2O_3, AZO, HfO2, IGZO, ITO, MgO, Mg-ZnO, Ta_2O_5, ZnO, ZrO_2
MEMS and NEMS	Sensing, actuation, acoustics	Al_2O_3, $BiFeO_3$, KNN, $LaNiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, PMN-PT, $SrRuO_3$
CMOS and power IC	High-k, passivation	AlN, Al_2O_3, CeO_2, HfO_2, MgO, $SrTiO_3$, TiN, ZrO_2,
Energy	SOFC, PV, batteries, thermoelectrics	YSZ, CIGS, Gd-CeO_2, ITO, $(La,Sr)(Co.Fe)O_3$, Li_xMnO_2, Li_xCoO_2, Na_xCoO_2, $Zn_{1-x}Al_xO$
Photonics	Electro-optics, IR-detection, waveguides	$BaTiO_3$, ITO, $LiNbO_3$, PLZT, $Y_3Fe_5O_{12}$, ZnO
Memory	Magnetics, spintronics	$BiFeO_3$, $CoFe_2O_4$, CrO_2 , LSMO, $MnFe_2O_4$, MnO
Metals and conductors	Electrodes, reflectors, alloys, superconductors, metal-insulator transition	Ag, Au, $Ba(Bi,Pb)O_3$, $LaNiO_3$, Ni, Pd, Pt, $SrRuO_3$, $SrLaCuO_4$, V_2O_3, $YBa_2Cu_3O_{7-x}$
Epitaxy	Templates, superlattices	CeO_2, GaN, $LaAlO_3$, MgO, $SrTiO_3$, TiN, YSZ

http://solmates.nl

evaporation hardware IV – ion beam assisted evaporation

many commercial evaporation processes presently employ ion bombardment of the substrate as a means of improving film properties.



An ion gun, typically generating ions with energies of a few keV, is used in conjunction with an evaporation source.

This process known as ion-beam-assisted deposition (IBAD), combines the benefits of high film depositionrate and substrate ion bombardment in a relatively clean vacuum environment.

Central to the technique is the generation of inert (e.g., Ar^+) and/or reactive (e.g., O_2^+) ion beams and their subsequent interaction with surfaces to modify film structure and composition.

We note that ions (~ 1 keV) impacting the growing film are considerably more energetic than arriving evaporant atoms (~0.1 eV). They serve to peen the surface and compact the film, densifying it in the process.

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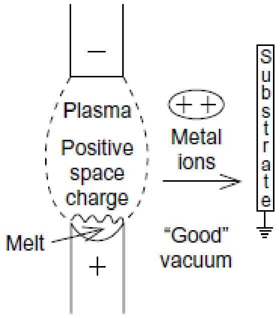
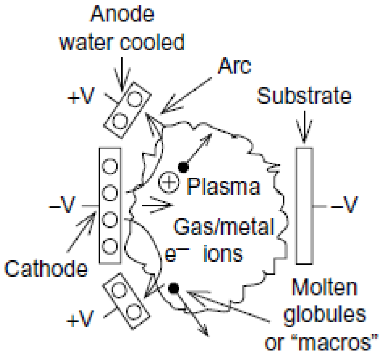
Arc evaporation

The first commercial use of the arc evaporation-deposition method was for TiN coatings deposited at low temperatures, particularly for high-speed steel cutting tools by arc evaporation of titanium in a nitrogen plasma.



(a) Vacuum arc



(b) Cathodic arc

Contray to ebeam evaporation Arc vaporization in a very low pressure vacuum occurs when a high current-density, low voltage electric current passes between slightly separated electrodes in a vacuum, vaporizing the electrode surfaces and forming a plasma of the vaporized material between the electrodes.

In order to initiate the arc, usually the electrodes are touched then separated by a small distance. On the cathode a "cathode spot" is formed that has a current density of 10^4–10^6 A/cm^2. The temperature at the cathode spot is extremely high (around 15 000°C), which results in a high velocity (10 km/s) jet of vaporized cathode material.

This current density causes arc erosion by melting and vaporization and the ejection of molten or solid particles. On the anode the current density is much less but can be sufficient to melt and evaporate the anode. A high percentage of the vaporized material is ionized in the arc and the ions are often multiply charged.

The cathode spot is only active for a short period of time, and then it self-extinguishes and re-ignites in a new area close to the original spot. This behavior causes the apparent motion of the arc.

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Industrial excursion: Evatec in Trübbach


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Optical Monitoring
UV to IR, monochromatic or broadband, test glasses or direct substrate measurement

https://evatecnet.com/

evaporation conclusion

Evaporation methods are perhaps the simplest means of producing thin films and coatings comprised of sequentially deposited atoms.

Thermodynamics, particularly source temperature-vapor pressure relationships, govern rates of evaporation and the nature of the vapor stream.

Film thickness uniformity is governed by the geometric placement of source and substrate. As long as the substrates are planar, the film thickness distribution can usually be modeled in terms of the laws of emission from point or surface sources, and substrate reception based on the inverse square separation distance between the two.

Film uniformity and coverage become more problematical over substrates that are stepped or contain trenches and other complex topographies.

The vacuum space and partial pressures of residual gases within it have an influence on film purity and properties such as resistivity, reflectivity, and hardness.

Evaporation techniques for thin-film deposition have been superseded in many instances by sputtering and CVD methods; difficulties in maintaining stoichiometry and achieving conformal coverage are among the reasons for this. Paradoxically, however, pulsed-laser deposition enables excellent stoichiometry to be attained in complex oxide films.

Despite shortcomings, evaporation methods are readily scalable to large operations such as web coating. However, in addition to conventional applications, the versatility of evaporation techniques is exploited in molecular beam epitaxy as well as other hybrid deposition processes. Arc evaporation is used for deposition of hard coatings.

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exercises

1) What are the different methods for melting the charge, and their advantages and disadvantages?
2) Explain how e-beam evaporation works
3) How is film thickness controlled in evaporation systems?
4) How can we control the mean free path of the vapor?
5) Explain the view factor, $1/r^2$ deposition rate dependence, and their impact on across wafer uniformity
6) Why is shadowing/step coverage a problem, and what can we do about it?
7) Explain the advantages and disadvantages of evaporation
8) How can tungsten be evaporated?
9) State the similarity and difference of arc evaporation with that of vacuum evaporation. How is the cathode spot characterised? How does the cathode spot split? What is meant by steered arc? State the challenges with arc evaporation deposition
10) State the similarity and difference of arc evaporation with that of vacuum evaporation.
11) How is the cathode spot characterized in cathodic arc evaporation?
12) Discuss possible interactions between the target material and the evaporation crucible. Propose solutions for circumventing these problems.
13) Let’s assume a standard chamber design where the evaporation source and the substrate are centered on the same axis and facing each other. Propose modifications in chamber geometry that can improve coating uniformity.
14) Zinc has a melting point of 420 C and a vapor pressure of 0.1 mbar at this temperature. To deposit a film by evaporation, is a melt necessary or would it also sublime?
15) An Al film was deposited at a rate of ~ 1 µm/min in vacuum at 25°C and it was estimated that the oxygen content of the film was 10^{-3}. What was the partial pressure of oxygen in the system?
16) A critical point dryer is used to remove liquid from delicate samples. It is sometimes necessary to circumvent damage caused by surface tension during drying. Discuss possible process flows that can achieve this and mark them on the PVT diagram.

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