Division 6 – Lincoln Laboratory
Massachusetts Institute of Technology
Lexington 73, Massachusetts

SUBJECT: PARAMETERS OF THE THIN FILM DEPOSITION PROCESS

To: Professor Ewan W. Fletcher

From: Peter Fowler

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Approved: _____
           Arthur L. Loeb

ABSTRACT:

        The formation and nature of thin films is considered from the
point of view of molecular kinetics of film and substrate. General
criteria for control of some properties of films are discussed.

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E. Fletcher

A. Loeb

W. Highleyman

The memorandum has been divided into the following section.

INTRODUCTION

A problem exists as to what materials, structure, geometry, etc., are required for the optimum thin film component. It is known that various solids with particular crystal orientations will have to be firmly deposited on different substrates. Reliable means for control of any combination of desired properties must be developed.

Experimentation to the present has shown that the difficulties attendant in just getting a vapor to deposit and remain on a surface are numerous. The first and foremost problem, then, arises in connection with intermolecular attraction and the macroscopic phenomenon of adsorption. Since Langmuir published his Nobel Prize winning theory[133] of monomolecular adsorption in 1918, many attempts have been made to obtain theoretical coverage of the phenomenon of multimolecular adsorption.[1,2,41,116,133-154]

Assuming that the deposit has been accomodated by the substrate, the question then arises as to what the structure of the deposit is, and how we can control it. A unified theory describing the process of crystal growth proceeding from multimolecular adsorption has not been published as yet, although Yang[49,50], et alia, have given some rate equations involving few unknown parameters.

This paper discusses observations made upon deposition of vapors of normal solids in relation to the forces involved and the molecular kinetics of the participating substances. Criteria for the choice of parameters which effect various properties are implied to some extent.

Section A.   FORCES OF ADSORPTION

The forces entering into physical adsorption are[1,2,14,24] listed below. The dependence of _energy_ of interaction on separation, r, of two particles is given in each case as r^{-n}. In general when one molecule is considered as interacting with a surface composed of molecules of the other type in question the dependence of interaction energy varies as $r^{-\sqrt[n]{n}}$.

    1. Dispersion (London)[3,129] fluctuating multipoles - Always
       attractive and orients molecules with greatest numbers of
       nearest neighbors.*

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* This force is the reason for different heats of adsorption on different crystal faces (varying surface density of molecules). Germer[31] endorses this view, but in Reference 1, pp. 760-64, Rhodin states objections.

    a.   Dipole - dipole; proportional to r^{-6}(by far the most important term at usual film equilibrium distances except for some polar substrates.)

    b.   Dipole - quadrupole; proportional to r^{-8}.

    c.   Quadrupole - quadrupole; proportional to r^{-10}.

2.   Repulsive (Exchange or Valence); proportional to e^{-r/r_o}, or r^{-n}, with n taken equal to 9 to 100 for various cases.[29]

3.   Vibration of solid lattice.

4.   Vibration of adsorbate.

5.   Internuclear molecular vibration.

In addition to these, polar substrates have forces acting which cause molecules to orient in a particular way, especially in the case of polyatomic molecules. These are predominant in some cases.

6.   Orientation (Keesom)[4] mutual attraction between permanent dipoles; proportional to r^{-6}. - Attractive or repulsive depending on orientation when adsorbed.

7.   Induction[128](Debye)[5] - Always attractive.

    a.   Mutual attraction between permanent dipole and induced dipole; proportional to r^{-6}.

    b.   Mutual attraction between permanent quadrupole and induced dipole; proportional to r^{-8}.

    c.   Mutual attraction between permanent quadrupole and induced quadrupole; proportional to r^{-10}.

In the case of ionic substrates, the surface energy for an adsorbate has been calculated as a function of distance from the adsorbent, including the effects of 1, 2, 6, and 7 above, using a summation process up to a distance $r = \rho^{-1/3}$, where ρ is the number of equivalent lattice points per unit volume, and thence integration assuming a continuous energy per unit volume. Other cases have been calculated also, especially by deBoer.[29] The minimum of the curve obtained gives the energy required to take the adsorbate from this equilibrium position to infinity with the exception of the effects of vibration (3,4, and 5 above). The physical surface is thus described by a 3 dimensional potential surface[70,130] which gives us the heat of adsorption at every point for a molecule at

its equilibrium position, being a periodic function for a perfect crystal. This is the type of model used in the study of epitaxy[7]. The effects of surface heterogenities (cracks, dislocations, etc.) has been investigated by deBoer and Custers[24] and Polyani[68]. They find that the variation of energy of adsorption for topographies varying from needles to needle-like cavities is of one order of magnitude[28] and thus could prove to be a great effect in adsorption. *

Section B.   MOLECULAR ADSORPTION KINETICS

        We have then that when a molecule strikes the "surface" of a solid, (the height of the surface dependent on the energy of the molecule), it may transfer some of its energy to the solid lattice, and thus be left with less than enough energy to escape the well. A molecule would thus remain in this site if not energized. This is the situation we have at low temperatures. The well that the molecule may be in though is possibly not the deepest one that the surface offers and therefore the binding of the molecule is not as strong as might be is we could get the molecule to migrate over the surface. ** The process that occurs to allow such lateral motion of the molecules is the quantized energy transfer of the solid lattice vibrations. These vibrations are dependent on the temperature and thus we see how temperature enters as a factor in the sticking of films. We may also see that this energy will be in opposition to the Van der Waal's well and thus the heat of adsorption will not be the depth of the well as we go to higher temperatures but will decrease according

*   The effect of electrostatic attraction and repulsion between ions and ionic substrates, tending to localize action over ion of lattice, has been neglected in the foregoing. This is of some importance in a few cases.[29,125]

**   A cluster of molecules that may by chance aggregate at some spot will undoubtedly become unstable and form a crystal structure in an attempt to get in a lower energy state. The absence of migration however, will not allow any sort of continuity of the film (i.e., any long distance ordering) but rather we may have a layer of random crystals. The active sites thus presented[29] will be of great adsorptive ability but we must balance this gain against our requirement, in some cases, for uniformity of structure.

to some law. Lateral motion due to incomplete transference of the kin-
etic energy of the arriving molecule is of importance also[69].

Assuming we know the potential variation of the surface due to
multipole effects and repulsive forces, we are thus led to consider the
process of surface diffusion which is required to situate molecules in
preferred sites. The motivating forces is as noted above - solid lat-
tice vibrations. Volmer and others[8,9,71,131] showed conclusively that
under certain circumstances, surface diffusion does take place. A famous
experiment due to $V_o$lmer, is the formation of crystals of Hg from vapor.
The crystals grew out of the substrate at a rate more than 1000 times that
calculated to be possible on the basis of direct addition of molecules
of the vapor to the crystals. Since we may assume that during a suf-
ficiently long period of time during the experiment, the atomic beam
deposits atoms uniformly over the surface then there is little question
as to the necessity of surface migration for the occurrence of this ef-
fect. Yang[50] states, however, that when some area of nuclei is presented,
direct impingement of atoms becomes an important part of the nucleation
process.

The quantum mechanics of the migrational process were investigated
for the case of gases by Lennard-Jones and others[11,18,23,56] assuming the
Langmuirian model of adsorption. They treat the vibration of the solid
lattice as the perturbation (derived from expansion of a Morse potential)
causing a surge of energy to and from the solid. The surges cause trans-
itions of the atoms to various energy states. Calculations made place the
time that a molecule will remain in such a state on the order of 10^{-12} sec.

Let us assume that an adsorbed atom (Becker coined "adatom"[21,22])
held by some potential well is given a quantum of solid vibrational energy.
The atom may then be excited to a higher bound level in the well or into
the continuum where it is either captured by another well or leaves the
surface completely. (Lennard-Jones[56] points out that a mobile atom may
also lose energy by collision with another mobile atom or bound atom.
If the energy of activation for migration is small compared with kT, then
collisions will be rare and if the concentration is not too large so that
migration is not prevented by other adatoms then theory indicates that the
mean life of activation will be nearly independent of temperature.)

We may assume that the momentum transfered to the adsorbate is dependent on the type of substrate and crystal face present. Thus, since the fact that whether migration or evaporation takes place is dependent on the direction and magnitude of vibration, then we should have certain substrates causing more migration, or evaporation, than others at the same temperature. The macroscopic parameters here are specific heat and total energy.

In addition, there will be a temperature dependence (of excitation) of both the number of quanta transferred per second and the energy of these quanta. There is a finite probability of 2 or 3 quanta being transferred simultaneously, but it is found to be negligible in our case. A possible mechanism for evaporation is the second order process of an additional quanta being transferred to the molecule while it is an excited state.

It is on this latter basis that Lennard-Jones calculated the mean life of the adatom in an excited state to be approximately 10^{-12} sec. He further calculated the time that a gas atom is expected to be in an adsorbed state and found it to be on the order of 10^{-5} seconds. This result is in agreement will the mean life $\mathcal{T}$ of an adatom found experimentally on the basis of Langmuir's theory. This carries the implication that the perturbation used in Lennard-Jones theory is by far the most important effect in the range of temperature and pressure used for confirming experiments.

The possibility that substrates rich in conduction electrons could cause excitations by means of the electron motion was investigated by Lennard-Jones. In metals we have approximately 10^{15} col./sec. of surface atoms with electrons so there is ample reservoir of energy for transitions. The calculation of mean time of transition is again approximately 10^{-12} sec., and the electrons are 1% efficient in this transfer. This then is not as large an effect as the former effects discussed but it is interesting that it will be independent of temperature and thus may be a dominant factor for transitions at low temperature.

Section C.   LATERAL INTERACTION AND MOLECULAR MOBILITY

The foregoing theory was developed for the explanation of gaseous adsorption. It is obvious that we must make some changes to apply these results to the adsorption of molecules of substances that are normally solid. (e.g., metals). A gas is characterized by slight attraction at large separation and by large repulsion at small separation, whereas normal solids have quite strong attraction at small separation. We must therefore, concern ourselves with lateral (adsorbate-adsorbate) interactions. (Lennard-Jones has given a good qualitative description of molecular cohesion[23]).

For gaseous adsorption, then, lateral interaction is negligible and, in fact, theories of monolayer coverage by adsorbed gases postulate that it is non-existant. However, the process of aggregation of adatoms from vapors of normal solids will make a continually decreasing portion of the surface available for true Langmuirian adsorption. In addition to the variation of the number of substrate adsorption sites we see that there will be attraction (or possible repulsion) due to the presence of the adsorbate itself. This situation then is not as simple to treat as gaseous adsorption, for instead of the molecules playing a more or less independent part in the adsorption, now each molecule is a source of energy, i.e., the molecule being adsorbed takes over the role of the substrate but with (in general) different adsorptive ability.

This adsorbate-adsorbate interaction will lead to the formation of crystals while the crystal growth will be modified by adsorbate-substrate interaction (termed lattice fit) and enhanced (or not) by vibrationally activated migration. The lateral interaction, if negative, may just compensate for the positive vibrational energy thus giving the depth of the multipole well (page 5) its physical meaning of heat of adsorption. That lateral interaction is important is apparent from the marked rise of heat of adsorption and peak at monolayer coverage; lateral interaction is expected to be pronounced when each molecule hitting the surface must find itself confronted with several nearest neighbors[26,27].

The general process of migration and evaporation of adatoms due to Lennard-Jones as described in Section B is undoubtedly that occuring with the adsorption of vaporized solids. We may draw a conclusion from the first

and second order processes of energy transfer noted in that section, namely:
there should be a discreteness in the phenomena of adsorbed films in the
following manner. Assume an atom to be captured by a well of depth W and
further imagine the transfer to the atom of a quanta of energy E corres-
ponding to the existing temperature. If $E > W$ the atom goes to the contin-
uum. If $E < W$ the atom goes to an excited bound state. In this case, the
second order process is required to excite to the continuum and this will
occur if $2E > W$. Now, if $2E < W$ but $3E > W$ (it is unknown whether the
third order process has been calculated) then the third order process is
required for excitation to the continuum. Now on the assumption that
migration is required for orientation of an adsorbed film, we see that as
$W = nE$ $n = 1,2,3$----we will have critical points for orientation phen-
omena. Since $E = f(T)$ there should be critical points for these phenomena
dependent on temperature.

There are experimental effects that may be explained on this basis;
for example, Rhodin's reorientation of aluminum films whereby the atoms re-
quire sufficient mobility (energy E above) to aggregate into crystals.[10]
That is, as Rhodin states, many deposited films are unstable in the sense
that a cluster of adatoms will aggregate in to crystal(s) provided that
the atoms have sufficient mobility. Brunauer (ref. 2, p.472) states that
kT must be raised so that it is as great as the energy difference between
the minimum and maximum potential sites.

Further, Rhodin's investigation of Aluminum deposition showed that
at lower temperatures, the (110) Al. plane was preferentially deposited
parallel to the mica backing. However, as the temperature of the substrate
is raised, there comes a point where the (111) plane deposited parallel
to the backing. It appears that lattice fit orientation must be modified
somewhat. On the lattice fit basis, the (110) plane should always be found
parallel to the substrate. We see than that a "critical" temperature ex-
ists above which the effects of the lattice fit are overcome by some other
force(s).

The above effect brings to mind the theory of Dixit[30]. He gives
a classical theory for such orientation based on the Van der Waal's equa-
tion of state for a 2 dimensional gas ($\pi A = RT$) and the Ramsey-Shields
equation (which gives surface tension as a function of temperature).

This argument shows that a given temperature corresponds to a particular area per adsorbed atom and thus to crystal planes of varying density. Assuming an amorphous substrate, Dixit was able to predict "critical re-orientation temperatures" for the deposition of various planes parallel to the substrate. The amorphous surface can be represented in our potential surface picture as a plane. Why not then assume that our crystalline structure approaches a flat potential surface with increasing temperature? The model that must be assumed contains no new forces but rather only the effect that vibrational energy pushes the potential wells up until we have effectively a plane surface. Experiments like those of Dixit on several substrates could prove the correctness of this. Rhodin states that the maximum orientation and rate at which orientation increases with temper-ature is typical of the substrate. This is what we would expect, since the potential surfaces of various substrates at the same temperature are cer-tainly different and the effect of heating of these different substances should not give the same rate of increase of vibrational energy (flatten-ing of the surface).

Dixit's theory shows that as temperature increases, each atom requires more area, i.e., the less dense planes of the crystal are deposited para-llel to the backing. If we assume, as is logical, that at the temperatures involved, formation of a crystal will proceed (migration is taking place and a crystal is a lower energy state than an amorphous cluster), then the mechanism that seems to determine orientation is that the surface is pushing as many atoms away from it as possible. That is, lattice vibrations would appear to be repulsing more adatoms as the temperature is increased and repulsing in such a manner as to allow only a low density of atoms to re-main parallel to the substrate. When enough atoms to form a unit cell aggregate these atoms will form into their crystal state with a plane par-allel to the substrate corresponding to the density of atoms determined by the above mechanism. Carrying this to its logical conclusion, we should have all molecules repulsed. The evidence for this is seen in the phen-omenon of evaporation at sufficiently high temperatures.

Rhodin's[10] investigation has shown that for higher substrate temperatures more oriented films are produced. We see, therefore, that since the effect of temperature is to increase mobility, then with more mobility the atoms

are able to reach more stable positions. This is in agreement with the earlier conclusion that for more mobile adatomic motion on a crystal substrate, the temperature must be such as to give the adatoms sufficient mobility to get out of the potential well. The smaller orienting forces (less stable orientations) should require lower temperature for such orientations to take place. This is found experimentally; a minimum kT is required for a particular orientation. König[46] showed that germanium films appear continuous when deposited on a substrate held at room temperature, but become granular when the substrate is heated during deposition. Sennett and Scott[47,57] found from electron microscopy that silver deposited at 70° to 300° C showed greater atomic aggregation than when deposited at room temperature. Heating of fast evaporated (2 seconds) films produced the same results. Bannon and Curnow[53] found that CaF_2 crystals grew from 170 Å to 250 Å as the temperature was increased from 100° to 300° C, necessitating atomic mobility. They noted different orientations appearing as the temperature was increased just as did Kubo and Miyake[54] in their investigation of Ca, Fe, and Ni deposited on PbS.

Levinstein[32] investigated the deposition of 35 metals. Results showed decreased orientation for substances of increasingly higher melting point. This is in agreement with Rhodin for if the substrate (amorphous) temperature kept constant and substances of varying melting points are deposited, the metals of lower melting point will have more mobility than those of the higher melting point, (the closer to the melting point - the more mobility). His results predict that a greater observed orientation should occur for more mobile atoms. If we were to raise the temperature of the substrate, we expect the metals of higher melting point to become moreoriented. Experimentation for proof of this effect was not carried out by Levinstein.

When we speak of mobility, it must be remembered that the motion will not be that of a perfect fluid, but rather more like that of a viscous fluid, i.e., mobility is characterized by short distance motions. That mobility is limited is pointed out by Schultz[52]. He shows that for an atomic beam obliquely incident, crystals grow inclined somewhat toward the axis of the beam thus demonstrating that the distance of mobile

motion is of the order of magnitude of the size of crystallites grown by him. Schultz also argues that since all crystallites at any time during deposition are of the same approximate height (even those growing from projections of the substrate) therefore mobility is limited, else one might expect some crystallites to be towering over others. The latter argument, however, is not sufficient to validate limited mobility since if one allowed completely free motion of all molecules one would expect something like a Maxwellian distribution of crystal heights which may be the distribution obtained. Cockcroft[37] showed experimentally the idea of some limited mobility by placing a wire near the substrate and noting that a few aggregates of the condensed vapor appear in the region of the wire's shadow.

In addition to the former effect, we would also expect the metals of higher melting point, if given enough mobility, to form more strongly oriented films since having a high melting point implies a stronger bonding or cohesive force, U. Semenoff[33] has shown the relationship of the energy of cohesion, U, (effectively the latent heat of vaporization) and the energy of adhesion, Δ, to the problems of deposition of films. He shows the critical pressure to be a function of temperature,

$p = a \exp(-A/RT)$ where $A = U + \Delta$ and a is a constant which depends on the geometry of the system, the size of the condensing particles, and a linear temperature correction. The quantity Δ is said by Rhodin to be the Van der Waal's energy between adatom and substrate and was experimentally found by him for aluminum films. We see then, that, as any of the attractive forces acting on an adatom increase, then the pressure of impinging atoms need not be as great for condensation to occur. Rhodin also found, as we could expect, that maximum orientation is greater for pairs of materials with greater A. Thus, in general, we might expect a more oriented crystalline film to be formed from the deposition of substances of higher melting point, dependent, of course, on the mobility imparted by substrate vibration.

Section D.   MOLECULAR VELOCITY

    The effect of varying velocity of atoms being deposited was inves-
tigated by Levinstein. Using a velocity selector apparatus, he was able
to find no difference in the size or structure of aggregates of the de-
posited metals. In the case of Antimony, a variation of size of aggre-
gates was found, but further investigation showed that this was due to
the presence of some polyatomic molecules of Antimony which naturally
would cause a different crystal size or structure than the monatomic
molecules.

    Bateson and Bachemeyer[51] attempted to explain poor deposits on the
fact that slow atoms were used for deposition. However, it would seem
that the velocity would be an indirect effect, the true factor being the
mobility of the atoms was so low that at concentrations (pressure) used
by them, well oriented aggregates could not be formed. The randomly or-
iented crystal atructure resulting would naturally provide for less or-
ientation in later layers than would a well crystallized formation.

    Beeck, Wheeler, and Smith[34] investigated deposition in gaseous
(.005 - 10 m.m. Hg.) atmosphere.* The collisions of beam atoms in tran-
sit form clouds and clusters of slow atoms before reaching the substrate.
The randomly oriented structure which formed in their experiments when
higher gas pressures (2-10 m.m. Hg.) were used could be explained by the
low mobility argument of the preceeding paragraph. In addition, it is
noticed that the presence of a gas of pressure .5-2 m.m. Hg. induces the
deposition of planes of low density parallel to the substrate implying
that this is the lower energy configuration rather than the planes de-
posited in vacuo. Levinstein[45] atates that there is no apparent reason
why this should take place. Beeck, et alia, suggest that the presence
of adsorbed gas would force the vapor atoms into positions corresponding
to planes of least density. They go on to say that the low density plane
phenomena occurs under conditions for which a complete surface layer is
highly improbable and thus the effect of gases on orientation must be

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* See also references 55, 86, 88-90, 162-4 for other experiments on de-
position in gaseous atmosphere.

purely kinetic, either through dissipating the condensation potential energy of the surface, or by effecting the energy distribution of the metal atoms before they reach the substrate. The answer to this problem can be partly answered when we know the mechanism that determines orientation of vapor deposits in vacuo. A good start would be constructive or destructive proof of Dixit's theory.

Miyamoto[40] gave a theory which implied a dependence of sublimation and condensation on the velocity of atoms. However, there appears to be an incorrect assumption. He postulated a "potential barrier" for sublimation (transition to continuum) much as was shown at the beginning of this paper but then goes on to postulate a barrier for condensation without giving the physics of such a barrier. Since the forces an atom is subjected to on approach to the surface are attractive and not until adsorbed does it meet the repulsive effects of temperature vibration, and other forces, then this assumption would seem false. The atom which is adsorbed (for a period as given by Lennard-Jones theory) comes to equilibrium with the surface, and in this state its velocity of approach is completely obscured. The deciding factor of the effect of velocity is experimental evidence and Levenstein's conclusion is that velocity is of no effect.

Section E.   RATE OF EVAPORATION

The fact that experimentalists may have concluded that velocity is a factor is probably because velocity and rate of evaporation are not independent. The effect of one could be mistaken for that of the other. Levinstein's investigation and qualitative theory shown the effect of rate of evaporation. That a "critical" pressure exists below which condensation does not take place has been shown by several[35-38]. It is the pressure at which point the rate of evaporation of adatoms is greater than their rate of arrival thus being due to the fact that substrate-adsorbate force is low. It is found in many cases that it is the presence of adsorbed impurities which partially satisfy and thus lower the substrates attractive potential.

Frazer[165] says that if a surface is completely outgassed, the vapors of most normal solids should experience no "critical point" even

with the weakest of substrate attractive forces. Many theories have been given covering "critical pressure" with particular reference to its temperature dependence including those of Frenkel[35], Fowler[41], Semenoff[33-126] Peierls[42], Devonshire[43], and reference 127. This variation with temperature is quite amenable to experiment (e.g., references 8,36-38,104-106).

All such theories depend in essence on the presence and magnitude* of the forces of physical adsorption discussed earlier although various methods of treatment are used. A high rate of evaporation however should be expected to have the same effect as a dense atomic beam of slow atoms, for both processes have the effect of putting atoms on the surface in great enough quantities for them to aggregate during their mean life . Levinstein's work shows that slow evaporation produces (for Antimony) large patches which have diffuse diffraction patterns whereas rapid evaporation gives smaller patches with sharp diffraction patterns (crystalline formation). He interprets the diffuse pattern as showing the Antimony to be in the amorphous phase. Levinstein further holds that we can not expect this to occur in general since the amorphous phase of many substances is not found probably because crystallization takes place so fast.

Beechnung[55] found that slow evaporation gives diffuse electron diffraction rings whereas fast evaporation gives sharp patterns. Deposition in gaseous atmosphere produced the same results. The rate of evaporation then effects the structure of the deposit by effecting the manner in which the molecular aggregates form and grow. Sennett and Scott[47,57] showed that rapidly evaporated (2 seconds) films tend to remain thin and cover the substrate more continuously as compared to slow evaporated (20 minutes) films which grow thick in well-defined aggregates before joining. They concluded from their experiments that normal migration time is interupted by the arrival of more atoms. The ensuing collisions are the means for nuclei formation. In 1937, Lennard-Jones[56] predicted a shorter migration time for gaseous adsorption than is given by his earlier quantum mechanical results. His conclusion was based on the fact that mobile atoms, when present in great numbers, will collide often leading to transitions to excited states or the continuum (whereas, in the case of

* For example, the statistical mechanical theory shows that as a greater lateral interaction (reaching to farthest neighbors) is assumed, the more definite is the critical temperature.

adatoms of normal solids, nucleation may take place instead). Their con-
clusion in terms of experimental parameters is that migration is a func-
tion of beam intensity, in addition to our earlier conclusion that it is
a function of substrate temperature.

Levinstein explains the preceeding phenomena as follows: The num-
ber of atoms in motion on the surface is proportional to the rate of
arrival of atoms and these adatoms will move over the surface until they
collide with other atoms and form patches (dependent on substrate forces,
especially the presence of cracks, impurities, dislocations, etc,).
Assuming evaporation has been in progress for a while with some patches
formed, the atoms arriving subsequently collide with each other to form
new patches or collide with old patches to increase their size. With a
high rate of arrival, the former event takes place since there is great-
er probability of hitting other adatoms than the relatively few patches.
With a slow rate of arrival, the latter event takes place since there is
greater probability that the mobile atoms will strike a patch before they
leave the surface and thus make fewer but larger patches. Carrying this
to its logical end, there will be a rate of arrival whereby the mean life

τ , of an atom in the adsorbed state, is shorter than the reciprocal
of this rate and thus condensation whould practically stop except for
some direct additions to the nuclei. Levinstein's experiment was con-
fined to Antimony and should we use a less mobile substance, the same ef-
fect might not be observed. By increasing the temperature, the mobility
could be increased and, therefore, the different effects noted for An-
timony might occur for these other substances also.

Sennett and Scott varied the evaporation rate of their deposition
by a factor of 2000 and yet the thickness of the film only changed by a
factor of 10. Evaporation rate then would appear to be a valuable para-
meter for varying the properties of films.

Section F.   **FILM THICKNESS**

Was[48] concluded that thin metal films are amorphous up to a cer-
tain thickness somewhere in the range 50 Å to 200 Å and at this point
crystallization takes place if temperature conditions are favorable.
His argument is based on:

      (1) the increase in conductivity of films at this point which he
          says follows from crystallization,

      (2) the fact that adhesive forces are stronger than cohesive for-
          ces in very thin films and thus the substrate forces prevent
          formation of crystals.

In reference to point (1) we may consider Sennett and Scott's in-
vestigation of the growth of metal films and in the region of 50-200 Å.
Electron micrographs show that the phenomenon that is taking place is
that small aggregates (.001-.01 microns) are joining together. We con-
clude that this is the phenomena that was called crystallization. Sen-
nett and Scott found that maximum adsorption of light at this point where
the aggregates begin to join. The voids that exist between aggregates
when the film is thin would be detrimental to conduction and thus as more
aggregates join together conduction would increase. Repeating Was' ex-
periment and using electron microscopy could clear up the point.

Concerning point (2), we agree that the first few atom layers of
film are strongly influenced by the substrate but contend that after
several atoms are deposited in close proximity, the lateral interaction
will lead to aggregation (granting that there must be sufficient mobility
allowed). Yang, et alia,[49,50] in developing their thermodynamic-statist-
ical theory of nucleation from the vapor phase concluded that a unit cell
aggregation is required for crystal growth. The unit cell is $<$ 10 atoms
for many substances and thus we see that only very small aggregates are
required before we could expect the transition of the film to go from
amorphous to crystal structure. Sennett and Scott did not define the
state of the aggregates that were present before the joining process at
50-200 Å but we would conclude that they were crystalline. Was' con-
clusion that the films changed from amorphous to crystalline then is
thought to be in error although the joining of aggregates may change the

type of crystal structure perhaps leading to long chains of oriented crystals.

As a confirmation of the state of very thin films we have the results of Germer and White[161] who show electron transmission patterns of films in the range of 3 Å to 780 Å thick, displaying random crystal structure-strong apparent even at 30 Å thickness. Schultz[52], investigating Alkali Halides was unable to get reflection patterns for films thinner than 100 Å, but transmission patterns showed random crystals with (100) planes parallel to the substrate. (The explanation for (100) orientation is given as the result of cube faces lying on a smooth surface.) Thicker films showed (111) orientation. Harris, et alia[162], investigating thermal stabilization of gold smoke deposits (prepared in inert gas atmosphere) suggest three possible structures for the films:

1. Each aggregate consists of a number of crystallites surrounded by disordered regions.

2. Each aggregate consists of a large number of smaller nuclei.

3. Each aggregate consists of a single crystallite having a non-equilibrium lattice. From energy considerations, an excess of vacant sites is the most probable type of lattice.

They point out that, (1), which is the probable structure at very low temperatures ($\sim 20^\circ$K) is untenable from the point of view of rate of approach to equilibrium and that x-ray diffraction rules out (2) in favor of (3).

Other structures that one might have to consider might be

1. random crystal structure with non-equilibriym lattice.

2. amorphous throughout.

An example of 2 in the literature is Levinstein's work noted on page 15 of this paper. Antimony was found to be one of the substances for which the amorphous phase can be formed during slow evaporation. We might take this substance as representative of one end of the scale of structure of thin films. Next on this scale would come the randomly oriented films and thence to the well-oriented films and this whole scale verying with film thickness as noted. An important contribution here would be an argument pointing toward the relation between this scale and a scale of molecular orbital shapes and energies or some other microscopic quality of the deposit.

Rhodin's[10] investigation of thin aluminum films shows a variation of observed percentage of orientation with film thickness. He graphed thickness against orientation and found maximum orientation to occur for a small finite thickness, the films becoming less oriented as more atoms are deposited. We must keep in mind that temperature is a big factor in the orientation and, in theory, proper temperature can produce maximum orientation even to a single crystal throughout the thickness of a film.

It is reasonable to believe that the maximum conductivity point, maximum adsorption point, maximum orientation point, and joining of the small aggregates in the experiments of Was, Sennet and Scott, and Rhodin are all closely related. To compare Was' and Sennett and Scott's work, we might vary the evaporation rate and measure conductivity at the same thickness for fast and slow evaporated films. Sennett and Scott show that the aggregates don't join for slower evaporation rates until a greater thickness of deposit is obtained and thus at a given thickness the conductivity could be expected to be lower for the slowly evaporated film.

An account of the probable kinetics of very thin deposits during the period in which nuclei form is given by Andrade[132]. Becker[127] has written in the kinetics of the formation of nuclei. McLauchlin, Scott and Sennett[158] have watched the formation of nuclei and aggregates in an electron microscope.

It is possible that as separate patches of crystals growing out over the substrate will have boundary dislocations[119] when they join, unless we provide the atoms with sufficient mobility. It has been found[39,25] that long distance ordering of structure can be promoted in very thin (discontinuous) films by means of deposition in an atmosphere of gas. For light vacuum deposition the thicker films begin to show long distance order (fibrous texture[44]). At liquid air temperatures this probably won't occur but as temperature is increased, more crystalline structure of very long distance order should appear.

A phenomena probably allied to specific heat has been noted by some in that certain substances can not be deposited beyond a certain thickness - let us say in the micron range, yet other substances can be deposited to millimeter thickness. If we imagine a molecule striking

a deposit of some insulator whereby the energy transferred is not dissi-
pated by conduction, then we would expect an elastic collision resulting
in the repulsion of the molecule. That a sink for the incident energy
is required has been demonstrated numerous times in the M.I.T. film
laboratory, of Professor B. Harris. A good electron conductor is used
for a backing for the film and good deposits are formed but if the back-
ing is not a good conductor then it is in many cases impossible to get
the vapor to stick.

Section G.   LATTICE FIT

The effects mentioned on page 8 of the lattice fit of the depos-
ited material with the substrate has concerned many (e.g., references 1,
7, 37, 49, 50, 58-67, 107, 116, 155, 156, 159, 169). Basically, we re-
quire a deposit to have a lattice spacing complementary to that of the
substrate. Naturally the spacing required for best accomodation is not
simply that of the substrate, but is dependent in the type of force that
is of greatest effect in adsorption of the particular adsorbate. As an
example, strong dispersion force will situate the molecule with the most
neighbors, whereas an ion will be attracted to a lattice ion (if the sub-
strate is ionic). The best fit of an adsorbate lattice then could be with
a spacing different from the interatomic spacing of the substrate. There-
fore, in considering lattice fit, we may not say (without investigation
of the forces acting in a particular case) that an adsorbate, deposited
on a substrate with identical lattice spacing, will be easily accomodated.

Some have concluded that the maximum difference of lattice spacings
that will still allow accommodation of a deposited film is approximately
15%. This again is dependent on the strength of forces of adsorption,
e.g., the adhesion of an ion to a metal substrate is very strong and may
accommodate a pair of materials with much greater than 15% difference.
An example of the determining factors of lattice fit is seen in the adsor-
ption of aluminum on rocksalt[10]. Aluminum (110) plane will fit within a
few percent in the (100) plane of rocksalt, the atoms residing in posit-
ions of maximum Van der Wall's attraction. It seems likely that if we
were to ionize aluminum and proceed with deposition there would be much

less accomodation due to the electrostatic attraction of Aluminum to the
Cl^- sites opposing the position with most number of nearest neighbors, etc.
Due to the fact that the aluminun lattice is so distorted in such a posit-
ion, little if any crystal structure would be expected at normal temper-
atures. (The situation expected for higher temperatures is discussed ear-
lier with reference to Dixit's theory). Each case of lattice fit orient-
ation must be judged on its own basis using as criteria the relative mag-
nitude of the various forces of adsorption, such as have been calculated
by deBoer[29].

Section H.   ELECTRON DIFFRACTION

There is some disagreement as to the effect of the electron
diffraction process on thin films. Definite evidence has been given that
the crystal (or amorphous) structure is changed by the electron beam[72-75,83-85]
and other equally conclusive evidence shows no change in the films so
treated[76,164]. The variable that must be taken into account when com-
paring the results of various experiments are:

1. Density of beam.

2. Energy of electrons.

3. Adhesive force of deposit to substrate.

4. Cohesive forces of deposit.

With regard to (3) we must realize that electron bombardment
of a physically adsorbed film may require very little energy to break the
bonding and allow mobility of the atoms, whereas the energy required for
disrupting a chemically bonded film may be considerable.

Harris, et alia[162], provide an example of (4) in their work on
the sintering of gold blacks. Gold smokes upon being heated stabilize and
change optical and electrical characteristics. The energy required for
diffusion of a lattice atom to the surface of the smoke is found to be
about 1/3 of the 27.5 kcal./gm. atom for diffusion in massive gold. We
expect that the energy transfer of electrons should produce the same effects
as heating did in this case.

We must make a careful comparison of the parameters noted above
when considering the results of electron diffraction experiments. For

instance, the experimenter with a high energy, high density beam im-
pinging on aphysically adsorbed, thermodynamically unstable film will more
than likely report structural changes in the film or at least a change in
optical and electrical properties.

Wright and Woods[167] investigated the decomposition of thin films
of various salts and oxides under slow electron bombardment. Decomposition
was measured by the change in secondary emission which occurred after
bombardment. It was found that the energy required for decomposition did
not agree with the heat of formation of the compound as predicted by some.
The energy for decomposition tended to agree with the optical absorption
energy. The mechanism of decomposition in some cases was concluded to be
the releasing of free holes and electrons which migrate to the surface
where thay may release atoms from the compound and thus change the cathodic
emission properties. In this article, the work of several experimental-
ists in this particular field are discussed. Bombardment of Barium Oxide
films is covered by Imai and Mizushima[171].

The use of electron diffraction for investigating crystal struc-
ture of films is covered in references 61, 77-83, 87, 124.

Section I.   CLEANING OF SUBSTRATE USING PARTICLE BEAMS

The preparation of substrate utilizing electronic or ionic beams
is found to be helpful[91-93,166]. The desired effect of these beams is to
drive off chemisorbed material such as gases, whose masking of surface for-
ces is well known[49,94-96,131]. Yang was to have investigated the effects
of such forces in 1954 but no data has been published as yet. In the
course of a symposium on vacuum evaporated films[97] at least 10 methods for
cleaning substrates were presented and all agreed that the final step should
be cleaning with a beam of charged particles. Possible mechanisms for the
process of this cleaning may be: (1) Local intense heating by the beam causes
a surge of energy ejecting the adatom, or (2) Direct satisfaction of a
chemisorption bond. Experimentation with variable density and particle en-
ergy beams could clear up this point.

The use of electron beams is said to be superior to the use of
beams of other particles. An ion beam could be detrimental in some cases

due to its reactive effect. Protons of sufficient velocity could form Hydrogen. Hydrogens energy of chemisorption is generally low enough so that heating drives it off quite readily. However, if one must wait for the substrate to cool before proceeding with deposition, the cleansed surface has time to become contaminated again.

Carr[93] describes the effects of electron beam treatment of Gold, which could be detrimental to vapor deposition. When Mercury vapor is deposited on such a surface it is adsorbed to all but points where the electron beam had fallen. Mr. K. R. Shoulders gives the interpretation that the beam had reduced various organic substrates present, possibly to carbon, thus presenting a low adsorptive spot compared to the gold surface.

A recent book by Holland[166] gives much good discussion of the cleaning processes. An important point that he discusses is the requirement for a relatively high pressure to exist in order for glow discharge cleaning to be used; this paradox leads us back to the requirement for particle bombardment as a final step in the cleaning process.*

Dr. A. L. Loeb describes a method for post mortem investigation of cleanliness of the substrate surface. Visible radiation is made incident on the film and the optical constants are calculated from transmission and reflection experiments. The system is then reversed so the light is incident on the backing and the optical constants recalculated. Disagreement of the 2 sets of optical constants obtained implies the presence of impurities at the interface. The theory of reflection and transmission of radiation by thin films and methods for analysis are given in the two articles by Harris, Beasley and Loeb.[168,169]

Section J.   CONDENSATION COEFFICIENTS

We now bring into the discussion the coefficient describing the ability of a film to be deposited. Knudsen[101,102] defined a Thermal Accomodation Coefficient as $\alpha = (E_3 - E_1)/(E_2 - E_1)$, where E_1 is the energy

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* An analogous paradox has been suggested by Shoulders. One must keep in mind when using "getters" that their vapor pressure may be greater than the amount of vacuum required.

the molecule possesses before striking the surface, E_2 is the energy it
would have if it were in thermodynamic equilibrium with the surface, and
E_3 is its energy after it leaves the surface. Much data is available
giving the accomodation coefficients for gases on solids (e.g., see ref-
erence 99). The simplicity of the process of gaseous adsorption compared
to that of evaporated solids due to the relative absence of attractive
interaction between gas molecules makes the definition and measurement of
accomodation coefficients quite possible.

For the chemisorption of gases, a sticking probability (or co-
efficient), S, is defined, it being the ratio, of the number of molecules
chemisorbed (by forces of about 10 times those of physical adsorption) to
the number of molecules physically adsorbed. Since the molecule is defi-
nitely bound in such a case, rather than hopping around as does a physic-
ally adsorbed particle, and since the activation energies for evaporation
and chemisorption are amenable to experiment, therefore, this coefficient
can be found. Becker[100] has given an expression for its temperature de-
pendence which agrees with experiment. Becker and Hartman [27] have qual-
itatively interpreted the coefficient to be the probability that the
physically adsorbed molecules will dissociate into its constituent atoms.
This interpretation can be seen to hold only for polyatomic molecules.
For any molecule the qualitative statement should be that S is the prob-
ability that the physically adsorbed molecule form a chemisorption bond
with the substrate. The monatomoc gases are then accounted for. In the
case of polyatomic gases it is necessary to break the molecule into its
constituent atoms before chemisorption takes place. Therefore, we see
from Becker and Hartmans statement that they assume that once the mole-
cule is broken up into atoms the probability for chemisorption of the at-
oms is 1. This is reasonable since when the molecule is present in the
form of its separated constituent atoms there are strong unsatisfied bonds
for the substrate to satisfy.

For the case of deposition of solids, a Condensation Coefficient
is postulated, defined as the ratio of the number of molecules remaining
on the substrate to the number of molecules striking the substrate. The
complexity of the events occuring and the fact that simplifying assumptions
(such as homogenous or periodic surface characteristics) do not closely

enough describe the surfaces investigated, does not allow as yet explicit expressions involing only known parameters. Devienne has made many meas- urements of the coefficients using radioactive tracer studies. A short summary with bibliography is given in reference 103. Continued experimen- tation along this line combined with study of crystal nucleation and growth[107-123,127,157] will lead to the determination and reproducibility of results as is now possible with Accomodation Coefficients.

Yang, et alia[49,50] have studied crystal nucleation and Conden- sation Coefficients. In addition to the rate equation for nucleation which they derive, they give data on varying condensation coefficients. Ref- erence 155 gives a plot of lattice fit against condensation coefficient which turns out to be linear and for 15 to 20% lattice fit the condensation coefficient is almost zero for their particular experimental conditions. The increase of condensation coefficient for increasing thickness of de- posit is explained as due to the increasing availability of "sinks" for crystallization after nuclei have formed. As was noted earlier, another effect present after a monolayer or so coverage is the fact that usually the cohesive force (which is prominent at this stage) is much greater than adhesive force. On page 473 of Reference 155 it is shown that the con- densation coefficient is greater for an increased crucible temperature. This is quite in line with Levinstein's conclusions, given earlier, where- by at low evaporation rates, the molecules have a greater probability of evaporating before aggregating. Yang discusses this effect throughout from the standpoint of supersaturation of the atomic base.

Section K.   CHEMICALLY BONDED FILMS

Throughout this paper the retention of the adsorbate by the sub- strate by chemical means has been little more than hinted at. This is due to the fact that references to this effect in the literature are scarce. In the course of conversation with thin film experimentalists, it has been noted that examples of probable chemical bonding are sometimes more appar- ent than the literature implies. This bonding is thought not to be the chemisorptive type whereby the adsorbent and adsorbate atoms retain their identity but rather the formation of a compound at the interface that acts

analogously to an "impedance match" between substrate and adsorbate. An example of this bonding is Chromium or Aluminum deposition on glass which is believed to form a metal oxide at the interface. The adhesion of these films to glass is far greater than that of the noble metals which would not be expected to form a compound at the interface. A simple quantitative measure of film adhesion is the "strip test" whereby an adhesive tape is plac ed on the film and while being stripped off the ease of removal of film from substrate is noted. Aluminum and Chromium are effected less by the stripping than are the noble metals.

A more precise qualitative measure of film binding is that used by Rhodin[5]. The critical pressure (lowest pressure required for films to form on substrate) for a temperature T is, as stated in Section C, $p = \underline{a}\ exp-(U+\Delta)/KT$. We make a plot of $\ln p$ versus $1/KT$. The slope of the curve then gives $(U+\Delta)$, the binding energy of the film on substrate (including the effects of impurities adsorbed at the interface). It is questionable whether this experiment would show up the binding energy for all (or any) chemically bonded films however, since the atoms may be adsorbed at first by physical adsorption means and possible after some finite time the chemical bond forms. The slope of the curve $\ln p$ vs. $1/KT$ would not therefore indicate the chemical bonding.

It would be of great assistance in discussing the possible forces acting to bind the film and in predicting film qualities such as reflectance, resistance, etc. to know the binding energy for each pair of materials. An experimenter in the optical properties of films would have an advantage if he knew that possibly an oxide or other compound existed at the film-substrate interface. The distribution of electrons and space charge which exists is intimately connected with the surface boundary conditions as is shown by Skinner[170]. A few binding energies are given by Wexler[172], having been compiled from the few references that the literature holds. A project which would possible be of great worth would be a more complete compilation of such data and an attempt at a classifying analysis of the data.

signed: *Peter Fowler*
                                                              Peter Fowler

PF/gk

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BIBLIOGRAPHICAL ABBREVIATIONS

Abbreviations for periodicals listed in the preceeding bibliographies are:

A.C.	Acta Cristallographica
A.d.P.	Annalen der Physik
C.R.A.S.	Academie des Sciences Comptes Rendus
D.F.S.	Discussions of the Faraday Society
J.A.C.S.	Journal of the American Chemical Society
J.A.P.	Journal of Applied Physics
J.C.P.	Journal of Chemical Physics
J.O.S.A.	Journal of the Optical Society of America
J.P.C.	Journal of Physical Chemistry
J.P.R.	Journal de Physique et le Radium
J.P.S.J.	Journal of the Physical Society of Japan
K.Z.	Kolloid Zeitschrift
P.C.P.S.	Proceedings of the Cambridge Philosphical Society
P.M.	Philosophical Magazine
P.N.A.S.	Proceedings of the National Academy of Science
P.P.S.L.	Proceedings of the Physical Society of London
P.R.	Physical Review
P.R.S.	Proceedings of the Royal Society of London
P.T.R.S.	Philosophical Transactions of the Royal Society
R.M.P.	Review of Modern Physics
R.S.I.	Review of Scientific Instruments
T.E.S.	Transactions of the Electrochemical Society
T.F.S.	Transactions of the Faraday Society
Vac.	Vacuum
Z.f.P.	Zeitschrift für Physik
Z.P.C.	Zeitschrift für Physikalische Chemie