

The Growth and Structure of Thin Metallic Films

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The structure of thin metallic films was studied by means of electron diffraction and electron microscopy. Microcrystal size can be correlated with the melting point of the metals, those with high melting points producing continuous films of small unoriented microcrystals while those with low melting points produce large microcrystals oriented preferentially with respect to the substrate. The effects of varying experimental conditions on the film structure of selected metals are reported. The electron beam of the electron microscope affects metals with low melting points most directly, producing melting, sublimation or crystallization. Variations in the velocity of the impinging atom, obtained by passing thermal atoms through a mechanical velocity selector, produce no effect for metals whose vapor is monatomic. Antimony whose vapor is found to consist of polyatomic molecules as well as atoms produces films whose grain size seems to vary with the size

of the molecules forming the antimony film. The rate of evaporation merely determines whether zinc or cadmium films may or may not be formed while for antimony films it also determines the type of the films formed. Those formed by rapid evaporation consist of small crystallites while those formed by slow evaporation consist of large amorphous patches. This effect is explained on basis of the mobility of the atoms on the substrate, the mobility time being determined to be less than 2×10^{-6} second. The mobility time and therefore the structure depends upon the type of substrate. The degree of vacuum is critical when the residual vapor reacts with the film being formed, but if no reaction takes place between residual vapor and film, pronounced variation for films formed in a vacuum are produced only when the pressure is above 10^{-2} mm of mercury.

I. INTRODUCTION

THIN metallic films formed by evaporation are characterized by properties which differ considerably from those of the bulk metal. Extensive studies on resistivities, for example, have shown that the resistivity of a thin film is considerably greater than that of bulk metal and that the ratio of resistivity of a film to that of the bulk metal depends upon the thickness and the type of film. Besides the variation in structure between bulk and film, there is considerable variation between films formed under varying experimental conditions. The variables which are most frequently cited as causes for conflicting results are the type of substrate, the temperature during deposition, the velocity and rate at which atoms hit the substrate and the degree of vacuum maintained in the evaporation chamber. Some of these factors have already been investigated. Picard and Duffendack¹ studied the structure of thin films by means of the electron microscope and found that films may be formed more easily on certain substrates than others. König² observed, by a combination of elec-

tron microscopy and electron diffraction, that germanium films which appeared continuous at room temperature, became granular when the substrate was heated during the evaporation. While it is quite tedious to study the effects of all experimental variables on all metals, it is desirable to determine which experimental conditions and which metallic properties are most likely to affect film structure. The most effective tools for such an examination at the present time are a combination of electron microscopy and electron diffraction. Electron diffraction alone cannot give any information on gross structure, except by deduction. While the size and shape of the microcrystals composing the film may generally be estimated from the sharpness of the rings, this method becomes unreliable in two cases. When rings are sharp this technique for measuring crystal size cannot be used to any degree of accuracy because of the uncertainties inherent in the method. When the rings are very diffuse it is often difficult, because of this diffuseness to determine whether the rings are produced by very small microcrystals or by a truly amorphous state.

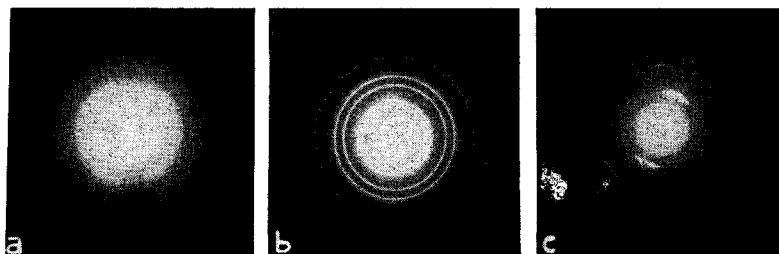


FIG. 1. Electron diffraction patterns of several metal films; a: high melting point metal; b: intermediate melting point metal; c: low melting point metal.

11

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¹ R. G. Picard and O. S. Duffendack, *J. App. Phys.* **14**, 291 (1943).

² H. König, *Reichsberichte f. Physik* **1**, 7 (1944).

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The electron microscope on the other hand can give no information about films made up of crystallites beyond the resolution of the instrument or about the structure of large patches of atoms. It is the object of this investigation to combine electron microscopy and electron diffraction in a systematic survey of thin metallic films and some factors affecting their structure.

II. THE EFFECT OF THE MELTING POINT OF A METAL ON THE STRUCTURE OF THE FILM

In order to determine which of the physical properties of metals determine film structure most directly, 35 different metals were evaporated on at least 2 occasions in a vacuum chamber at pressures not exceeding 0.01 micron. The films were condensed on a collodion substrate. A range of film thicknesses for electron diffraction studies was obtained by placing several collodion films at different distances from the atom source. For electron microscope examination it was found more convenient to obtain variations in film thickness in such a way that one picture could show the entire range of thickness desired. This was accomplished by placing a razor blade over half the collodion film. Then at the razor edge the penumbra effect due to the extended atom source produced the required variation. It was found that the films studied could be classified in three groups, according to their characteristics.

Group 1: Metals showing diffuse diffraction patterns. Of the metals evaporated the following can be placed in this category: tungsten, tantalum, iridium, columbium, rhodium, germanium, silicon. Of these all but germanium and silicon have a melting point above 1900°C. Figure 1a shows a typical diffraction pattern of a metal in this group. The deposits of all metal films in this group were found to be crystalline, since the ring spacings agreed with those computed from x-ray data on crystalline bulk metal. Had the diffuse rings been caused by an amorphous deposit, different spacings would have been obtained. The crystal size was estimated to be less than 15Å. This did not vary appreciably with increased film thickness. As might have been expected from the diffraction pictures, electron microscope pictures showed continuous films for all film thicknesses.

Group 2: Metals showing a sharp line diffraction pattern without preferred orientation. This group includes gold, silver, copper, nickel, iron, cobalt, chromium, manganese, titanium, beryllium, lead, tin, palladium, and platinum. The melting point of these substances with the exception lead and tin are between 600 and 1900 degrees centigrade. It was generally found that for extremely thin films, the diffraction rings were diffuse. They sharpened, however, with increased film thickness. Films with

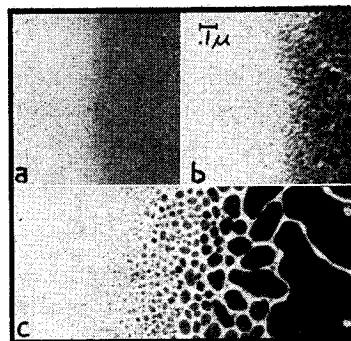


FIG. 2. Electron micrographs showing variations of film structure as a function of thickness for a: high melting point metal; b: intermediate melting point metal; c: low melting point metal.

melting points over 1300°C appeared continuous in the electron microscope. Those with a lower melting point were granular. This subdivision is somewhat artificial, however, since it depends upon the resolving power of the electron microscope and to some extent upon the film thickness. Figure 1b shows a typical diffraction pattern of a film in this group. All patterns in this group were identical with those of Germer³ and others.

Group 3: Metals producing films whose microcrystals are oriented with respect to the substrate. The following metals are included in this group: antimony, bismuth, tellurium, cadmium, zinc, magnesium, indium, thallium. Thin films were obtained easily for all metals in this group with exception of cadmium and zinc. Methods for forming films of the latter two metals will be discussed later. Without exception these substances have melting points below 650°C. Electron microscope examination of the films generally showed small crystals for thin films growing into large islands for thicker films. Figure 2 shows this behavior for indium compared with the behavior of metals in the other two groups under similar conditions.

Of the metals in group 3 antimony was studied most carefully. Electron diffraction studies by several observers^{4,5} have shown that antimony

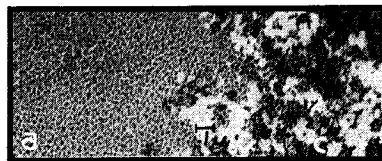


FIG. 3. Partially crystallized antimony film. Region a is amorphous. Its electron diffraction pattern shows diffuse rings. Region c is crystalline. Its diffraction pattern has sharp rings.

³ L. H. Germer, Phys. Rev. **56**, 78 (1939).

⁴ J. A. Prins, Nature **131**, 761 (1933).

⁵ F. Richter, Physik. Zeits. **19/20**, 406 (1943).

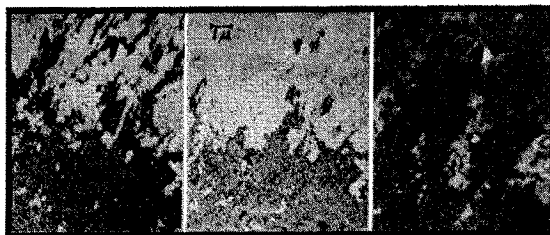


FIG. 4. Apparent variation in the structure of antimony films. The three pictures show the same field of view as the film is turned slightly with respect to the electron beam.

exists in an amorphous as well as a crystalline state. Electron diffraction studies do not in any way indicate the gross structure of antimony films. It is impossible to determine from diffraction pictures whether the amorphous phase is homogeneous or composed of patches of atoms. An electron microscope examination is therefore necessary. Figure 3 shows a partially crystallized film of antimony, the region marked *a* is amorphous, giving diffuse diffraction rings, the region marked *c* is crystalline with considerable preferred orientation. It is interesting to note that the size of the patches in the amorphous region is identical with that in the crystalline region. In the electron microscope the regions differ only in the degree of transparency. The patches in the amorphous region seem homogeneously semitransparent while those in the crystalline region are either completely transparent or opaque. This variation in density or thickness is found to be nonexistent upon closer examination and appears to be due to the crystallinity and preferred orientation of the small patches in region *c*. The effect is similar to that observed by Hillier and Baker⁶ on chromium smoke. A microcrystal appears opaque either when it is so thick that electrons cannot pass through it, or when it is so oriented with respect to the electron beam that electrons after being reflected from a particular set of crystal planes cannot pass through the lens system of the microscope. The latter seems to be the case here. Figure 4 shows this effect even more strikingly. All pictures represent the same field of view. The apparent change was produced by chang-

ing the inclination of the specimen with respect to the electron beam between exposures. This effect confirms the deductions by Williams and Wyckoff⁷ from stereoscopic pictures of antimony films. For fairly thick crystalline films of antimony several types of preferred orientation were observed. When each microcrystal is oriented with respect to the substrate but not with respect to the other microcrystals, continuous rings of anomalous intensities are obtained. These rings break up into arcs when the film is tilted in the diffraction camera. Frequently when microcrystals touch each other, crystallization of one affects the crystallization of the others and together they form one large antimony crystal or several smaller ones. This is shown by the patterns in Fig. 5. The high degree of preferred orientation may also be observed when a thick film tears. Breaks occur along straight lines, making angles of 127 degrees with each other (Fig. 6).

III. THE EFFECT OF THE ELECTRON BEAM ON THE STRUCTURE OF THIN METALLIC FILMS

One of the inconsistencies in electron diffraction studies is produced by the heating effect of the electron beam. This effect is small for substances with high melting and boiling points, but rather noticeable for the others. Substances in group 1 did not change while they were being examined. Of the metals in group 2, gold in particular was observed to change by electron bombardment. Continuous films of gold appeared to granulate when they were exposed to a strong electron beam for a short time. Most metals in group 3 were affected considerably by electron bombardment. Zinc and tellurium sublimed without melting (Fig. 7). In the case of tellurium the thicknesses of the individual crystals did not change during the sublimation process. Holes in the film merely grew bigger, one crystallite evaporating after the other. Zinc crystals on the other hand changed in thickness while the other dimensions remained unaltered. The residue observed is probably an oxide shell which remained after the zinc had evaporated.

Figure 8 shows the effect of the electron beam on thallium films. Thallium melted when first exposed

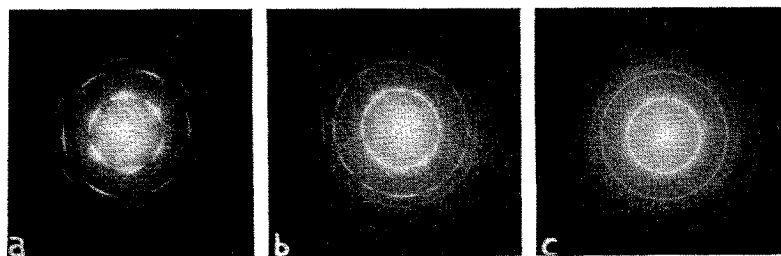


FIG. 5. Varying degrees of preferred orientation in antimony films. In film *a* the microcrystals are oriented with respect to each other, producing a single crystal. In film *b* the microcrystals form several smaller crystals. In film *c* microcrystals are still oriented with respect to the substrate but not with respect to each other.

⁶ J. Hillier and R. F. Baker, *Phys. Rev.* **61**, 722 (1942).

⁷ R. C. Williams and R. W. G. Wyckoff, *J. App. Phys.* **15**, 712 (1944).

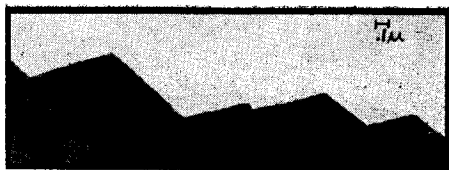


FIG. 6. A broken film of antimony, indicating a high degree of crystallinity.

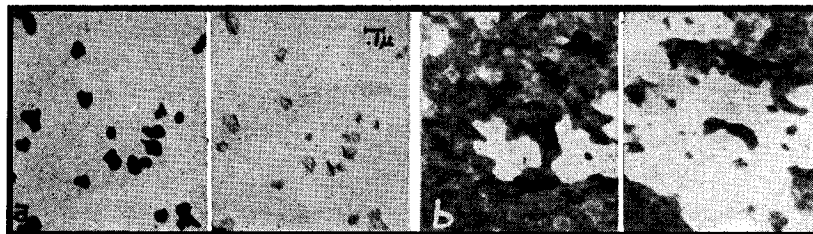
to the electron beam. The liquid droplets which were formed later evaporated under additional electron bombardment. Indium on the other hand, because of its relatively high boiling point, melted without showing evaporation of the liquid droplets (Fig. 9a). Thin antimony films which were always amorphous, crystallized after some electron bombardment. This process of crystallization revealed itself by the apparent change in density of the previously homogeneous patches composing the film (Fig. 9b). Actually the gross structure of the patches did not change; antimony atoms did not leave the patch, but merely rearranged themselves.

IV. THE EFFECT OF ATOMIC VELOCITY UPON CRYSTAL STRUCTURE

It has been suggested by various observers that the velocity of the impinging atoms might have a considerable effect upon the types of film formed. Miyamoto⁸ has developed a theory according to which a potential barrier at a surface would permit only fast atoms to reach the surface while slower atoms would be reflected. Beek, Smith, and Wheeler⁹ have suggested that preferred orientation of films, formed by atoms evaporated in a gaseous atmosphere, might be caused by the decreased velocity of the atoms after colliding with the gas atoms. Bateson and Bachmeyer¹⁰ have attributed the poor quality of some evaporated nonreflecting coatings to atoms of low velocity. In order to study the possible effects of atomic velocity on the film structure a mechanical velocity selector was constructed. It consists of a duralumin cylinder into which helical grooves are milled (Fig. 10). As the cylinder rotates, atoms pass along a groove without

hitting the ridge only if they move in the proper direction with the proper velocity. Atoms can reach a collector directly opposite the source only if they have a velocity equal to the pitch of the helix times the angular velocity of the rotating cylinder. Collectors placed ahead or behind the central collector receive faster or slower atoms, respectively. It is thus possible to obtain a complete velocity distribution during one evaporation. This type of selector has several advantages over the more commonly employed slotted disks or rotating drums.^{11,12} It makes it impossible for particles in the vapor beam to reach the collector simply by moving at a sub-multiple of the desired velocity. These particles hit the ridges between the grooves. Secondly it makes possible short evaporation times, since the ridges between the grooves may be made quite thin, and as great a fraction as 80 percent of the atoms evaporating with the proper velocity may reach the collector. The rotor is placed into a vacuum chamber which is then evacuated to a pressure of 0.002 micron. The metal to be evaporated is placed either in a tungsten filament or an alundum oven in front of the rotor (point A, Fig. 10); the collector consists of several collodion films placed at the rear of the rotor (point B, Fig. 10). In order to maintain a clean vacuum even as the apparatus becomes warm during a long run, it is necessary to avoid the more conventional type motor, with insulated wire or other parts which outgas upon being heated. The rotor is driven by means of magnetic pulses supplied by an electromagnet outside the vacuum. A band painted alternately reflecting and nonreflecting (C in Fig. 10) is pressed around the dural cylinder and an iron bar (D) is attached to the rotor-shaft. Outside the vacuum chamber is a light source and a photoelectric cell, connected by means of an amplifier to the electromagnet. With the rotor turning, pulses of light are reflected from the bulb into the photo-cell producing, in turn, a series of pulses in the electromagnet, thereby driving the rotor, as a motor with a "photoelectric commutator." The selector thus speeds up until the energy fed into

FIG. 7. Sublimation of metals produced by the electron beam of the electron microscope. a: Zinc at the beginning and at the end of an examination; b: Tellurium at the beginning and at the end of an examination.



⁸ S. Miyamoto, *Trans. Faraday Soc.* **29**, 794 (1933).

⁹ O. Beek, A. E. Smith, and A. Wheeler, *Proc. Royal Soc.* **A177**, 62 (1940).

¹⁰ S. Bateson and A. J. Bachmeyer, *Nature* **158**, 133 (1946).

¹¹ J. A. Eldridge, *Phys. Rev.* **30**, 931 (1927).

¹² I. P. Zartman, *Phys. Rev.* **37**, 383 (1931).

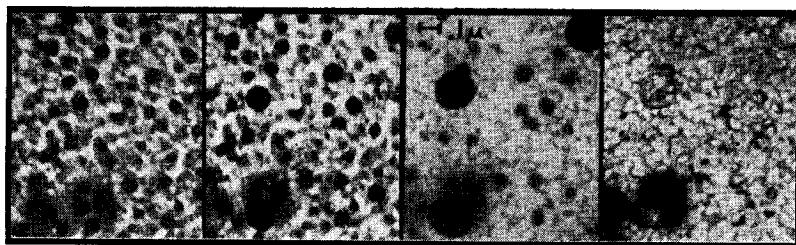


FIG. 8. A sequence of four pictures showing the melting and evaporation process observed during a study of thallium films.

the system equals that dissipated in the bearings. The speed at which the system rotates depends upon the power per pulse supplied by the amplifier, the duration of the pulse as determined by the ratio of the reflecting to the nonreflecting portions of the rotor ring, and the position of the iron bar with respect to the electromagnet when it is energized. The rotor is self-starting, since a small pulse produced by turning on the light source produces sufficient excitation. The speed is determined by means of Lissajous figures on an oscilloscope. Speeds as high as 15,000 r.p.m. are obtained without special effort.

Metals in groups 2 and 3 were studied by means of the velocity selector. Those in group 1 were not included in the study because of their extremely high boiling points and the resulting high velocities. Of the metals in group 2, gold was selected and of those in group 3 antimony and bismuth were chosen.

Gold

The velocity spectrum for gold agreed with that expected on the assumption of a Maxwell-Boltzmann distribution for a monatomic gas. The structure of gold films depends upon thickness as has been mentioned previously. In comparing films of equal thickness formed in high and low velocity regions, no variation was observed either in appearance or in crystal structure.

Antimony

Seven evaporations of antimony through the velocity selector were performed. For six of these it was observed that the patches in the high velocity regions were considerably smaller than those in the low velocity regions. Figure 11 shows a typical velocity selection for antimony. Patches in the high as well as the low velocity regions were examined by electron diffraction and found to be amorphous. It was further observed that the distribution curve was not one which might be expected from monatomic antimony vapor with an atomic weight of 122. Assuming a Maxwell-Boltzmann distribution, the molecular weight was calculated to be about 300. This indicates that antimony in the vapor phase consists of polyatomic and diatomic molecules and perhaps some atoms. The

deposits in the low velocity region of the velocity spectrum are thus produced mainly by polyatomic antimony molecules, while those in the high velocity regions are produced mainly by atoms and by some diatomic molecules. Since the patches in the low velocity regions are formed by fewer but larger molecules than those in the high velocity regions, there are fewer, but larger nuclei of condensation in the low velocity regions than in the high velocity regions with the resulting fewer but larger patches. It seems highly improbable that the variation in size of the patches is due to variation in the velocity of the impinging atoms.

Bismuth

Bismuth is known to exist, in the vapor phase, as a mixture of atoms and diatomic molecules. It may therefore be used to determine whether the variation in deposit structure which was observed for antimony is characteristic of antimony or whether it exists for other metals with a similar type of vapor. Three evaporations of bismuth were performed. The deposits were found to differ considerably from those of antimony, even though the crystal structure of the two metals is the same. Films in the high as well as the low velocity regions were completely oriented, and there appeared no variation in crystal size. The type of vapor is thus not the only factor involved in determining variations in gross structure.

The above experiments seem to indicate that velocity variations within thermal ranges do not affect the structure of the metal films. This may not necessarily be the case when velocities are much higher. High velocities were obtained by charging a 1 μ f condenser to 15,000 volts and then discharging it through a 1 or 2 mil wire, thereby exploding it. Under these conditions, however, fragments of metal as well as atoms fly into space. The fragments were found to embed themselves in the substrate. Similar results were obtained by passing a high current through a tungsten filament. Figure 12 shows an electron microscope picture of such a fast evaporation at high temperature. A metal droplet ejected by the filament embedded itself in the previously formed film, leaving a crater. Atoms which were evaporated later cast a

shadow of the droplet, thereby recording the order of events.

V. THE EFFECT OF THE RATE OF EVAPORATION ON THE STRUCTURE OF THIN METALLIC FILMS

From theoretical considerations the rate of evaporation may be expected to have a considerable bearing upon film structure. It has been shown by several observers¹³⁻¹⁵ that when the vapor beam density is below a certain critical value, films cannot be formed. This critical density is a function of the substrate temperature and varies widely for different metals. Frankel¹⁶ has explained this by assuming that atoms arriving at the substrate move over the surface and eventually re-evaporate from the substrate. When a collision occurs between two of the atoms which are moving on the surface an atom pair is formed which has a much longer lifetime on the surface than a single atom. Such pairs then act as nuclei of condensation. The critical beam density thus depends upon the lifetime of a particular metal atom on a particular surface. Metals in group 3 showed the greatest dependence upon rate of evaporation. Zinc and cadmium films could not be formed at all at low rates of evaporation. When the rate of evaporation was high, films were formed quite readily, but as might have been expected, control of film thickness under these conditions was difficult, and films prepared by this method could not be used for transmission electron diffraction work. For intermediate rates of evaporation isolated zinc and cadmium crystals could be observed similar to those reported by Picard and Duffendack. If evaporation continued long enough, a film was eventually formed with these crystals as nuclei. These effects might be expected for other metals if the substrate temperature were raised, permitting re-evaporation of the atoms, before relatively stable atom pairs might be formed by mobility of the atoms on the surface. Antimony because of its anomalous behavior was studied in detail. While this behavior is not characteristic of many metals at room temperature, it affords an insight into film formation. Figure 13a shows an antimony film evaporated at a low rate (less than

1 atom layer per second), while Fig. 13b shows a film of the same thickness evaporated rapidly.

The large patches of slowly evaporated antimony produce a diffuse diffraction pattern, while the smaller patches of rapidly evaporated antimony produce a sharp ring pattern. This indicates quite clearly that the large patches obtained by slow evaporation are of the non-crystalline form of antimony also observed in very thin films. Five amorphous antimony films were examined periodically over a period of several months. Some crystallization occurred in all films. In two instances there was preferred orientation. In three instances crystallization without orientation was obtained (Fig. 14). No other method was found for obtaining un-oriented antimony films by evaporation in a high vacuum.

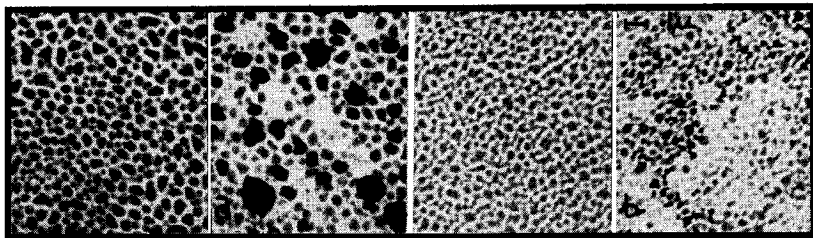
It appears from these observations that the rate of evaporation affects the crystal structure only indirectly by affecting the grain size of the deposit. When antimony is evaporated rapidly, small patches are formed which at first exhibit no crystalline properties. They are, however, highly unstable in that form, and crystallize rapidly when sufficient atom layers are present to overcome the disordering influence of the substrate. Patches which are formed by slower evaporation, thereby covering a larger substrate area, are much more stable, and crystallize only slowly if at all.

The dependence of particle size on the rate of evaporation may be explained by expanding Frenkel's concept of surface mobility. Two additional assumptions must be made.

1. The number of atoms in motion on the surface is proportional to the number of atoms arriving at the surface per unit time.
2. Atoms or molecules will move over the surface, until they suffer a collision with other atoms or molecules and thereby lose their mobility.

Let us assume that evaporation has been in progress for some time and that there are a certain number of atom patches on the substrate. Newly arriving atoms may either collide with these patches, thereby increasing their size, or collide with each other, thereby forming new patches and increasing

FIG. 9. The effect of the electron beam on the structure of indium and antimony films. a: Two pictures of an indium film. The first was taken just as the film was exposed to the electron beam, the second after some electron bombardment. b: Two pictures of an antimony film. The first shows an amorphous antimony film, the second shows the same film partially crystallized by electron bombardment.



¹³ R. W. Wood, *Phil. Mag.* **32**, 364 (1916).

¹⁴ J. B. Chariton and N. N. Semenov, *Zeits. f. Physik* **25**, 287 (1924).

¹⁵ J. D. Cockroft, *Proc. Roy. Soc.* **119**, 295 (1928).

¹⁶ J. Frankel, *Zeits. f. Physik* **26**, 117 (1924).

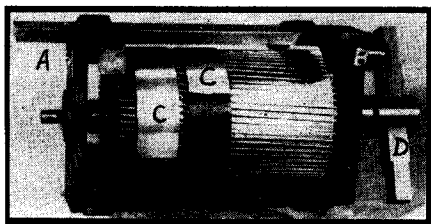


FIG. 10. Velocity selector for neutral atoms. A: location of oven. B: location of collodion collectors. C: Rotor band. D: Iron bar used to drive the selector.

the number of the existing patches. If the rate at which atoms arrive at the surface is high, the latter is the case, since the probability for collisions between migrating atoms is greater than that between atoms and already existing patches. Thus many small new nuclei are formed. If atoms arrive at a slow rate, they will more frequently collide with the already existing patches, thereby increasing the patch size. This then results in fewer, but larger patches.

This variation in patch size suggests a method for estimating the length of time atoms remain mobile on the surface. If atoms are evaporated through a rotating slotted shutter disk, they will arrive on the substrate in pulses. The width of a pulse depends upon the width of the slots in the disk and upon the rotational speed. Figure 15A represents an idealized plot of the number of atoms arriving at the substrate *versus* time. Figure 15B shows the same relationship when the motor is turned at half speed. Then more atoms reach the surface per pulse, but there are correspondingly fewer pulses. If the average mobility time of the atoms on the surface is long compared to the pulse time, but much shorter than the time between pulses as shown by line a, then from the previous discussion particle size for case A should be greater than for case B, since there are fewer particles in motion on the surface when the disks are turned faster. Should the mobility time on the other hand be short compared to the pulse time (line b) the number of atoms in motion on the surface would be the same for case A and B, and the particle size would be the same in both cases.

An alternate procedure is available. Rather than changing the rotational velocity of the disk, the slot size of the disks may be increased and the rate of evaporation correspondingly decreased. Then

again the number of atoms reaching the surface over a long time interval is the same in both cases. If now the mobility time is long compared with the pulse time (line a, Fig. 16) the patch size will be the same for cases A and B', since the same number of atoms are in motion on the substrate in both cases. If on the other hand, the mobility time is short compared with the pulse time, patches obtained for case B' are larger than for case A. The second method may thus serve as a check on the first. If in the first method patch size remains the same, then it must be different in the second, and vice versa. The experiments were performed first with a disk of 2 slots, then with a disk of multiple slots. The disks were driven by the drive used in conjunction with the velocity selector. The shortest pulse time available was 2×10^{-5} second.

The most difficult problem encountered during the experiments consisted of holding the rate of evaporation constant, repeating the evaporation at the same constant rate later, and varying the rate of evaporation between wide limits. The oven found most useful for the experiments consisted of a tightly wound helical tungsten coil of about 1-cm length and $\frac{1}{2}$ -cm diameter. One end of the coil was closed with a tantalum shield. About 5 g of antimony in form of a cylindrical slug was surrounded with mica and fitted tightly into the coil. Preliminary experiments were performed to correlate the amount of material evaporated with the current through the coil and the amount of material received on the collector disks. The amount of deposit was determined as follows: A collodion film containing antimony patches was "shadow-cast" with uranium and photographed in the electron microscope. The number of antimony patches and their dimensions could then be determined. Films having an average thickness of as low as 0.1A were measured by this method. It was found that if no atoms were permitted to reach the collector during the initial heating of the filament, the rate of evaporation remained constant until about $\frac{3}{4}$ of the antimony had evaporated from the basket. For the actual experiments it was thus only necessary to set the filament current to an empirically determined value and weigh the antimony sample before and after each run. On several occasions when the amount of antimony evaporated did not agree with the amount expected from the current settings the run was repeated with a new

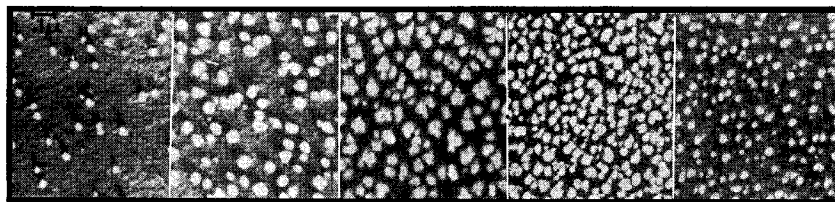


FIG. 11. Antimony patches formed by molecules of varying velocities. The velocity of the molecules forming these patches increased from left to right. The pictures are negatives of antimony films which have been shadow-cast.

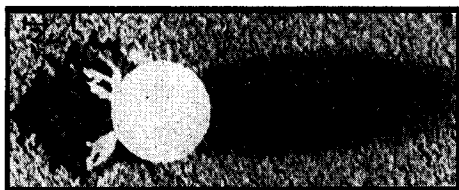


FIG. 12. Result of a rapid evaporation of gold. The small droplet (diameter 1.0 micron) was ejected by the filament forming a crater at its left. It then acted as an obstacle to the atoms evaporating later from the source, thereby producing a shadow at its right. The picture is a negative.

antimony sample. At least two runs were made for evaporation times of $2\frac{1}{2}$, 5 and 10 minutes and a series of pictures was taken of various sections of the collodion films.

The results obtained were entirely consistent. Using the first method the patch size was the same for cases A and B; for the second method larger patches were obtained for case B' than for case A. This indicated that the mobility time for antimony on collodion was less than 2×10^{-5} second.

The large extent to which mobility of atoms on the substrate affects the structure is more clearly born out, when the substrate is changed. Figure 17a shows antimony on gold. Here the rate of evaporation does not affect particle size, the microcrystals remaining of uniform size for all rates of evaporation. This is probably due to the fact that antimony atoms react with gold and remain at the place they originally hit. Great care must be taken in these experiments against contamination by organic substances, since they seem to affect the surface mobility of the atoms considerably. Figure 17b

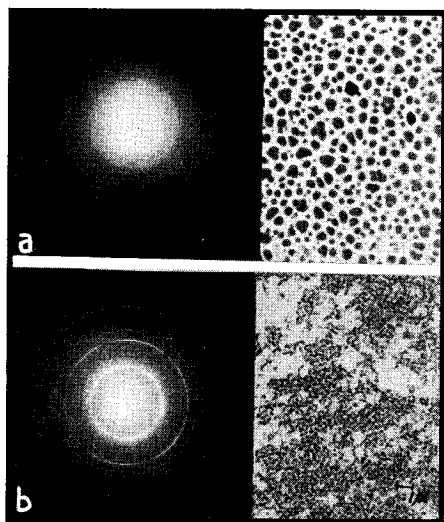


FIG. 13. Antimony films formed by varying rates of evaporation of antimony. a: Electron micrograph and electron diffraction pattern of slowly evaporated antimony which is amorphous; b: Electron micrograph and electron diffraction pattern of rapidly evaporated antimony which is crystalline.

shows such a surface which had been purposely contaminated by stopcock grease. Patch size varies considerably, and definite conclusions cannot be drawn from such a picture.

It must be emphasized here that the effects observed for antimony cannot be used to generalize for all metals. The amorphous (noncrystalline) state has never been observed for most metals. This could either mean that it does not exist or that crystallization taken place so rapidly that it cannot be observed. The variation in patch size which has been observed for antimony cannot be observed for most other metals at room temperature on collodion because of their low mobility. Raising the substrate temperature might produce the same effect

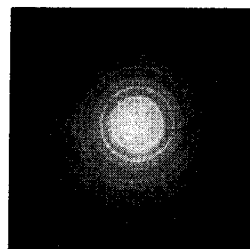


FIG. 14. Unoriented antimony film produced by the crystallization of slowly evaporated antimony.

for other metals. However a competing factor would then enter which could not only mask the observations but produce exactly the opposite results. If the difference between the melting point of a metal and the substrate temperature is small, the small patches which are formed may remain in the liquid state for considerable time and several droplets close together might unite to form a large crystallite. If evaporation is rapid there is a high probability that patches are still in a liquid state, when they come close to each other. For slow evaporation, solidification will have taken place long before patches have grown big enough or plentiful enough to touch each other and the crystallites will remain separate. The crystallites formed by rapid evaporation would then be larger than those formed by slow evaporation.

VI. THE EFFECT OF THE DEGREE OF VACUUM ON THE STRUCTURE OF THIN FILMS

The type of film obtained in a chamber only partially evacuated should be expected to depend upon the type of reaction taking place between the metal evaporated and the residual gas present. The residual gas may affect the film as it is being formed on the substrate or it may affect the individual atoms in transit from source to substrate. What takes place depends upon the pressure of the residual gas, that of the metal vapor and the

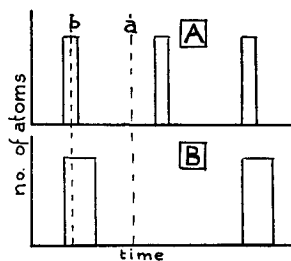


FIG. 15. Idealized plot showing the number of atoms arriving at the film surface *versus* time. A: Rotating slotted disk turning at full speed; B: Rotating disk turning at half speed.

degree to which chemical reactions may take place between the two. In general it is difficult to determine which of the two produces the observed effect. However, two extreme cases may be considered. When the residual gas is a metallic vapor which may form an intermetallic compound with the metal evaporated, a reaction may take place at the film surface even when the pressure of the residual gas is low. In that case the type of film being condensed and the type of residual gas rather than the pressure of the residual gas are the determining factors. Figure 18 shows such a reaction between zinc and gold. Zinc was evaporated slowly from a filament such that no zinc film could be formed, since the zinc immediately re-evaporated. When gold was evaporated simultaneously, however, a film was formed which showed peculiar configurations. Electron diffraction studies indicated a compound. This behavior is also pronounced when mercury vapor is present in the evaporation chamber. Since the pressure of the residual gas is extremely low it is highly improbable that any reaction between residual gas and metallic vapor could take place while the atoms move from the source to the collector.

The other extreme is the case when a residual gas which does not react with the metallic vapor is used at high pressure. In this case the vapor is not atomic but consists of a cloud of particles which seems to originate near the filament. The gas in this case affects the metallic beam in transit by producing collisions between the individual atoms before they reach the collector, so that the material reaching the collector consists of clumps of atoms. For pressures between 10^{-3} and 10^{-6} mm the results are somewhat inconclusive. An electron microscope examination showed no variation in structure as the pressure was increased to 1 micron. The most striking results were observed when zinc and cadmium were evaporated at a pressure of 0.01 mm. Figure 19, a and b, shows a comparison of zinc films formed in a high vacuum with those formed in a poor vacuum. The films formed in a poor vacuum had a mirror surface and their structure

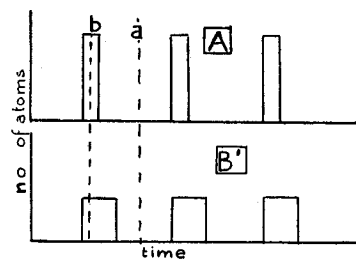


FIG. 16. Idealized plot showing the number of atoms arriving at the film surface as a function of time. This method provides a check on the method indicated in diagram 15. A: Maximum atom beam density, minimum slit opening in shutter disk; B: Atom beam density one half of maximum, slit opening in shutter twice the minimum value.

was very uniform. Such films were very suitable for electron diffraction study. A possible explanation of this may be given on basis of Frankel's hypothesis. When zinc atoms arrive at the collector they remain on the surface for only a short time and reevaporate before sufficient other zinc atoms arrive to make film formation possible. When the pressure of the residual gas is increased, collisions between individual metal atoms take place in the vicinity of the filament, thereby producing aggregates of atoms which have a much greater lifetime on the substrate than atoms. These aggregates act as nuclei for other atoms and thus make film formation possible. When the pressure of the residual gas is increased, the number of collisions between metal atoms further increases, resulting in the blackish deposit for most metals. These deposits for most metals appeared very much alike in the electron microscope (Fig. 19c). An interpretation of this structure does not seem possible. It appears, however, that the deposits consist of an array of particles which form near the filament and possess little mobility on the substrate. Electron diffraction study proved useful. Metals which generally showed preferred orientation when evaporated in a high vacuum, showed no orientation when evaporated at pressures of about 0.1 mm. Substances which had produced a sharp line diffraction pattern

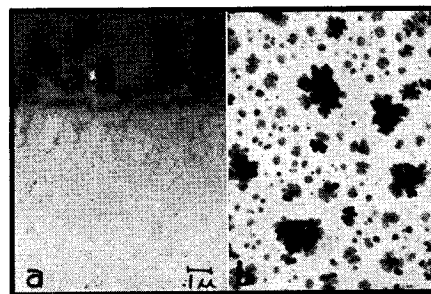


FIG. 17. Dependence of film structure on substrate. a: Antimony evaporated onto a thin layer of gold; b: Antimony evaporated onto a film contaminated with stopcock grease.

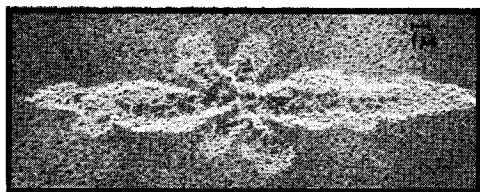


FIG. 18. Film formed by the simultaneous evaporation of zinc and gold.

when evaporated in a high vacuum showed diffuse rings when evaporated at 0.1 mm. Those which had shown diffuse rings at low pressures continued to show diffuse rings at 0.1 mm. This seems to indicate that for metals in group 1 the particles produced near the filament do not vary considerably in size from those formed on the substrate in a high vacuum. For substances in group 2 particles formed at the filament appear considerably smaller than crystallites formed on the surface. The lack of preferred orientation for particles in group 3 is fairly apparent, and this is understandable, since

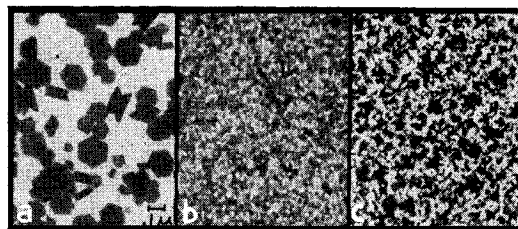


FIG. 19. Dependence of film structure on pressure. a: zinc evaporated at 10^{-5} mm of mercury; b: zinc evaporated at 0.01 mm of mercury; C: zinc evaporated at 0.1 mm of mercury.

there seems to be no physical reason as to why small crystallites falling onto a surface should line up in any particular way.

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