

METALLIC FILM FORMATION AT LOW TEMPERATURES¹

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Received September 23, 1946

Apparatus and method for condensing, under approximately isothermal conditions, thin films from a molecular beam of pure lead at temperatures down to 14°abs are described. The electric conductivity of these films is measured *during* and *after* exposure to the beam.

The onset of conductivity depends upon the temperature of the film formation and is found for hydrogen temperatures at a statistical film thickness of only two atomic layers.

After exposure these films undergo substantial changes, which depend upon temperature and are determined by two mutually opposing trends: (a) destruction of film coherence by coalescence into isolated globules of lesser thermodynamic configuration potential—predominant *above* 100°abs.; (b) transition into a molecular configuration of higher conductivity—predominant *below* 100°abs.

The results, in particular with respect to the nature of trend (b), are discussed in the light of hypotheses by Kramer and Suhrmann and one suggested by the authors.

I. GENERAL CONSIDERATIONS

The properties of thin films of metals deposited *in vacuo* center mainly around the problem of the stability of molecular (or atomic) configuration under the varying predominance of surface forces which counteract the attainment of the thermodynamically most stable arrangement of the molecules in more or less perfect crystalline array.

Consequently, in each particular case the properties depend to a very large degree upon the conditions under which the films are formed and subsequently observed. Since the properties of such films are dependent upon the relative stability of a particular molecular configuration on a surface of physically and chemically different nature (not dissimilar to adsorption phenomena), the temperature at which the films are formed is of major importance. It follows that in order to maintain quasi-stable film configurations for study and observation, such investigations should be preferentially conducted in the low-temperature range.

It has been the purpose of the investigations summarized in the following to investigate film properties from this particular point of view.²

¹Presented at the Symposium on Low-Temperature Research which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

²These investigations were conducted at this laboratory during the period 1931–41 and are described in detail in the Ph.D. theses and published articles listed below:

Anderson, A. B. C.: "Resistivity and recombinations in extremely thin metallic layers," 1933.

Foster, M. G.: "Conductivity and mobility of thin lead films," 1939.

Armi, E. L.: "Electrical conduction and crystallization phenomena in thin lead films at temperatures between 14°K. and 500°K.," 1941.

Foster, M. G.: Phys. Rev. **57**, 42 (1940).

Armi, E. L.: Phys. Rev. **63**, 451 (1943).

While extremely thin films can easily be produced by a variety of methods (chemical, electrochemical, cathodic sputtering, etc.), only deposits from the vapor phase, i.e., from a molecular beam under the purest possible vacuum conditions, are known to permit reproducible results which can lend themselves to interpretation.

In the existing literature of the field there are numerous indications of the extreme delicacy of such films, manifested by changes of properties caused by exposure to radiation, electron impact, and even small electric currents through the films; hence serious consideration has to be given to the physical means by which the properties of such films can be measured, so that disturbances of the film structure by the process of measurement are avoided as much as possible.

The determination of the electric conductivity with the use of minimal current densities (electrometric methods) has therefore been used, because it is the possibly least disturbing means of observation and also represents a singularly sensitive tool for the registration of alterations in film configurations. On the other hand, the obvious disadvantage inherent in the indirectness of the indications and consequent uncertainty of interpretation is somewhat compensated by the unusual sensitivity, since conductivity changes involving factors of 10^9 or more can be observed within short time intervals under sufficiently carefully controlled experimental conditions—an order of magnitude rarely available in measurements of other physical properties.

In view of these considerations, the experimental method and procedure were designed in the following studies to fulfill a number of desiderata: (a) The metal deposits should be formed at low temperature by condensation from the vapor phase (i.e., from a molecular beam). (b) The temperature at the surface at which the condensation occurs, i.e., the temperature at which the deposit is forming must be defined and measurable, at least approximately. (c) The rate of condensation must be so low that an adequate transfer of the thermal energy of the arriving molecule through the surface of condensation is accomplished in order to keep the temperature of film formation constant and as low as possible (isothermal condensation). Constancy and uniformity of beam configuration and intensity (number of arriving molecules per unit time and area) must be accomplished in order to permit the determination of the average thickness of the deposited film. (d) The surface upon which the film is formed must be of reproducible nature. (e) The possibility of determining conductivity variation continuously over an order of magnitude of 10^9 is required.

II. APPARATUS AND PROCEDURE

The vacuum vessel within which the metal was evaporated and subsequently condensed was arranged vertically (figure 1). The lower half contained furnace, collimator arrangement, and a magnetic shutter for the molecular beam, while the upper half supported the cryostatic assembly for the condensation. This glass vessel was about 50 cm. long and 9 cm. at the widest part, and the beam path had an approximate length of 15 cm.

The metal was evaporated from a furnace which had been specially designed (modification of construction previously published (4)) to maintain a uniform temperature throughout the furnace and the metal and had considerable heat capacity (thermal stability). It carried in the center of the metal charge an insulated thermocouple permitting the determination of temperature near the evaporating metal surface in the working range between 400° and 600°C .

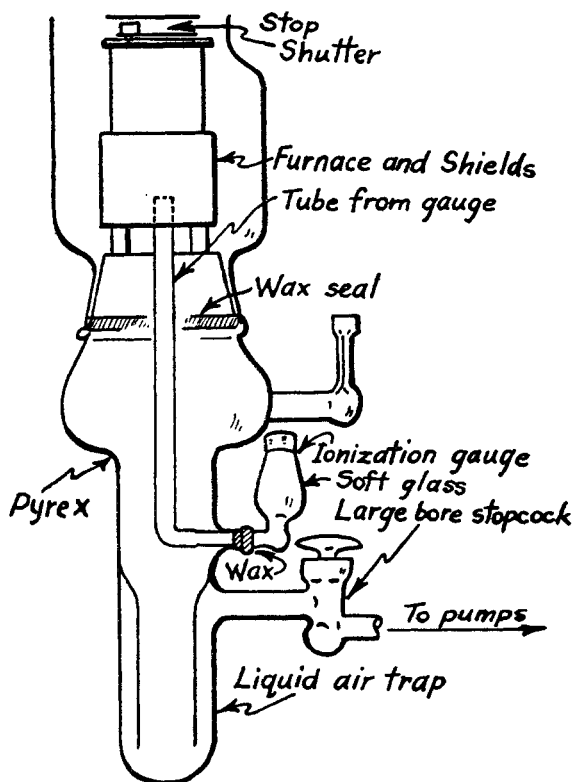


FIG. 1a

FIG. 1. (a) Schematic section through lower part of vacuum vessel. (Note: the tube leading to the ionization gauge is close to the furnace as the most probable source of residual gases.) (b) Schematic section through furnace, shield, and shutter assembly.

This furnace was encased in a tubular shield in order to restrict the molecular beam to the area of condensation, without exposing the latter to the penumbra of the beam. (The latter precaution is necessary in order to avoid the possibility of inhomogeneity.) This collimating device carried also a magnetically operated shutter which, when closed, protected the condensation plate positively against impact by random molecules evaporated from the furnace.

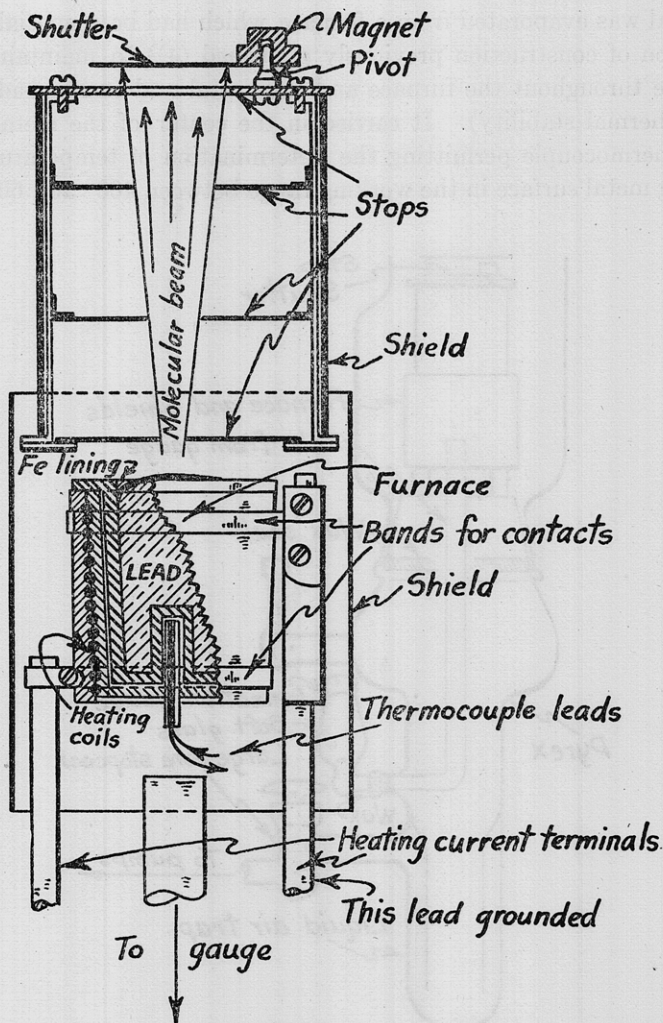


FIG. 1b

Considerable pains had to be taken in order to fulfill conditions (b) and (c).³

³As a base for condensation thin glass slides (micro coverglass 0.15–0.20 mm. thick) were used and were put through the customary rigorous chemical procedure of cleaning. The somewhat difficult but very significant establishment of very good thermal contact between plate and cryostat was accomplished by soldering a thin plate of cast iron (thermal expansion coefficient similar to that of the glass used) to the copper bottom of the cryostat and by soldering the other side of this plate (after copper plating to produce adequate anchorage for the solder) to the glass plate, the back of which was previously platinized and electrolytically copper plated. The soldered joint between the glass and cast-iron backing was produced after final outgassing and evacuation of the whole apparatus by means of heating with high-frequency induction.

The cryostat consisted of a thin-walled copper container with flat bottom to which the above condensation assembly was attached. This container was suspended in the vacuum vessel by a long thin-walled German-silver tube through which it could be filled. This tube was attached to the vessel by a large ground metal cone arranged for water circulation in order to prevent thermal strain at

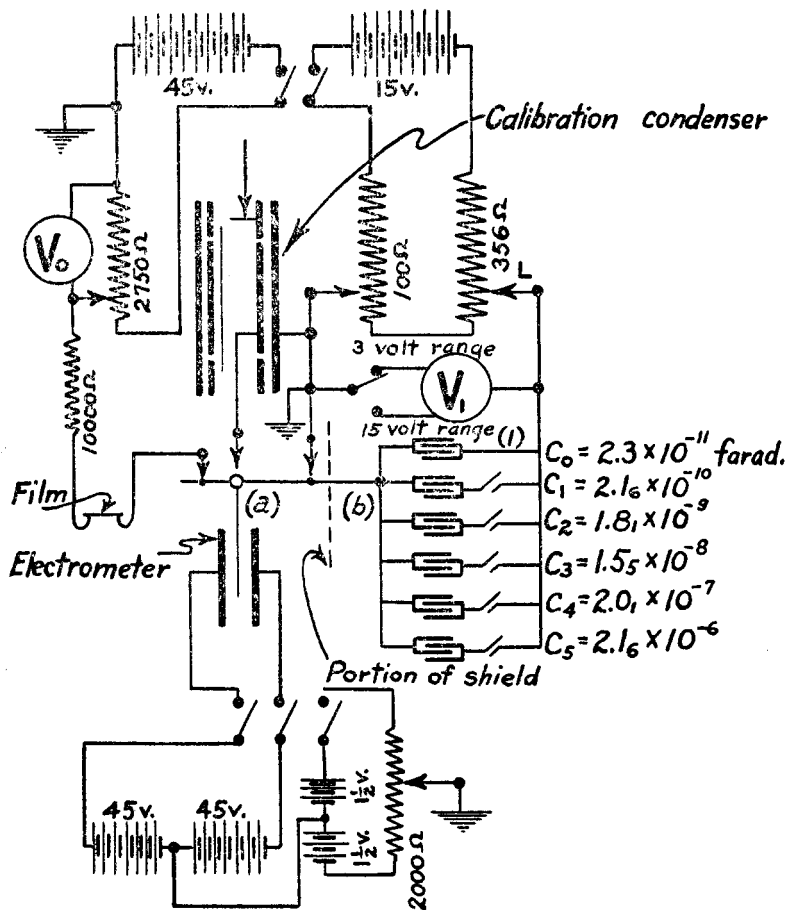


FIG. 2. Circuits for measurement of film resistances

the junction between metal and glass by transfer of cold from the evaporating cooling agent.

The cryostat could be connected through a Dewar siphon with containers for liquid air or hydrogen, and was also equipped for the reduction of the boiling temperature by lowering the pressure.

The electric contact with the film was made by platinizing sections of the exposed side of the glass plate, leaving only an area of 2 cm.² free for the section of the condensed film on which the conductivity was measured.

It was also considered a matter of major importance to shield the surface, particularly during the outgassing period, against condensation of impurities, and this was accomplished by applying a second shutter in front of the glass plate. A thermocouple at the plate made it possible to measure approximately the temperature changes occurring during exposure to the beam.

The method for measuring the electric conductivity was as follows (figure 2): A known potential E_1 charged a known capacity C by leakage across the film. An opposite potential, E_2 , compensated the charge of the condenser and a sensitive string electrometer was used as null instrument. One or more of a set of six condensers with capacities ranging from 10^{-11} to 10^{-6} F could be inserted into the circuit so that a change in conductivity over the order of magnitude of 10^9 could be measured almost continuously and in short time intervals. The resistance of the film is then given by: $R = tE_1/CE_2$.

The equipment for and the procedure of evacuation and outgassing were designed and manipulated in the manner customary for avoidance of disturbance by residual gases, especially by their condensation at parts exposed subsequently to low temperature. The vacuum was measured with sensitive McLeod and ionization gauges; the outgassing of the whole apparatus, in particular of parts of it, was accomplished with induction from a 10-kilowatt high-frequency source.

As metal for the formation of the films lead of high purity was used. The reasons for the choice of lead were:

(1) Its melting-point and vapor-pressure curves are particularly convenient, for an adequate rate of evaporation can be obtained without resorting to high temperatures which would seriously interfere (by radiation from the furnace) with the temperature conditions at the film surface during exposure; at room temperature the vapor pressure is sufficiently low to prevent stray condensation within the apparatus.

(2) The high specific gravity of lead permits a fairly accurate determination of the mass of heavy deposited layers for purposes of calibration by weighing.

(3) Because of the high molecular weight and large atomic volume of lead, it can be expected that the molecular mobility at the surface of the condensation is relatively small.

(4) Lead belongs to the fourth group of the Periodic System, where most elements are characterized by the existence of conducting or non-conducting allotropic modifications and where the electron configuration is favorable for superconductivity (in view of the possibility of extending these experiments into the range of helium temperatures).

The rate of film deposit as a function of furnace temperature and length of exposure interval can be derived approximately from kinetic theory considerations for effusing molecules under mean-free-path conditions in a high vacuum. While the calculation was found to result in the proper order of magnitude—a result which indicated the absence of appreciable reflection from the surface—an actual calibration was found necessary by weighing (microbalance) film deposits formed over a long period of time under constant conditions. It was found that at a furnace temperature of 400°C . the density of the molecular beam

(in g./min./cm.²) was 10^{-9} , at 500°C. 10^{-7} , and at 650°C. 10^{-5} , indicating that it was easy to arrive at a rate of condensation of the order of one (statistical) atomic layer per minute at the condensation surface without resorting to delicate thermal controls of the furnace temperature.

The experimental procedure consisted—after careful evacuation and out-gassing, extended over days—in bringing the furnace to thermal equilibrium at the temperature required for the desired rate of deposition. The cryostat was then cooled to the temperature required for film formation with liquid air and liquid hydrogen (if necessary under reduced pressure) and the “background” conductivity of the condensation plate was determined, which amounted to approximately 10^{14} ohms. The shutter in front of the plate was then opened and finally also the shutter of the furnace shield, so that the surface was exposed to the molecular beam while conductivity measurements were taken. After a sufficient number of atoms had been deposited, the shutter was closed and the changes which the film so deposited underwent with time at constant or varied temperature of the cryostat were followed by observation of the conductivity.

III. RESULTS AND DISCUSSION

In describing the results one has to distinguish between the conductivity observations obtained while the plate is exposed to the beam and those after the beam is shut out and the film is left to itself.

While there is common agreement among the investigators that a certain statistical thickness is required for establishing a conductivity, the magnitude reported for this quantity varies substantially with different observers who worked under approximately the same conditions. The values depend obviously upon the temperatures of formation of the film. Those found for lead are about 60 Å. at room temperature and approximately 30 Å. for liquid-air temperature, if rates of deposit of the order of 1–3 Å. per minute are employed. If the temperature of formation was in the range of the hydrogen temperatures, this thickness decreased substantially and conductivity was observed even at a thickness as low as 7 Å., equivalent to a statistical thickness of only two lead atoms (figure 3).

The conductivity of these exceedingly thin layers is instantly destroyed if the temperature is raised into the range in which tendency (a) prevails (see below). After, by such treatment, the conductivity is “wiped out” and the original low temperature is restored, a new layer can be formed on the surface without observable interference by the former layers. This operation can be repeated many times.

The conductivity behavior of the films *after* exposure to the beam depends upon the temperature at which the film is formed and the number of atoms contained in it, as well as the temperature to which the film is exposed subsequent to the closing of the shutter.

Films after exposure showed principally opposing tendencies:

(a) At a temperature above 100–120°abs. the trend is to form a non-conductive

configuration (if the low-temperature film is sufficient to show conductivity initially). If such films are left to themselves, the conductivity disappears quickly until the resistance reaches infinity (background resistance). Subsequent exposures to the beam show the same phenomenon repeatedly, until a total (statistical) thickness is reached which is many times that of the thickness which first showed conductivity.

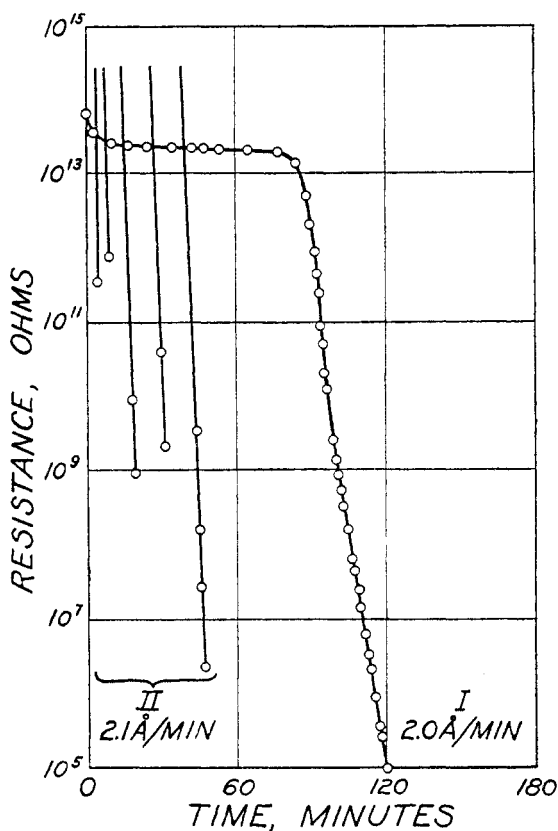


FIG. 3. Time-resistance variation during film formation: I at 290°abs.; II at 14°abs. I shows that about sixty statistical atomic layers (160 \AA .) are necessary to establish the beginning of conductivity; II that at 14°abs. conductivity sets in as low as two statistical atomic layers (7 \AA .) and that it can be "wiped out" and reestablished repeatedly (five times in this case). The parallelism of II indicates reproducibility without interference by previous deposits.

The rate of disappearance of conductivity decreases with increasing number of deposited molecules. The conductivity of the film reappears and disappears upon additional exposures to the beam at a rate depending upon the magnitude of the preceding deposits and rates of condensation until a thickness is reached which maintains its conductive qualities. This thickness again depends on the temperature at which the measurement is taken and is the larger the higher the temperature.

Figures 4 and 5 represent typical demonstrations of this behavior. Figure 4 (room temperature during and after exposure at a rate of deposit of about two atoms per minute) shows complete disappearance of conductivity up to film thicknesses of seventy to eighty atoms (230 Å.), while films formed at and subsequently exposed to 90–120°abs. at a lesser rate (less than one atom per minute) do not lose their conductivity any more completely for film thicknesses of about twenty atoms (50 Å.), while the trend towards a decrease in conductivity *after* exposure still persists.

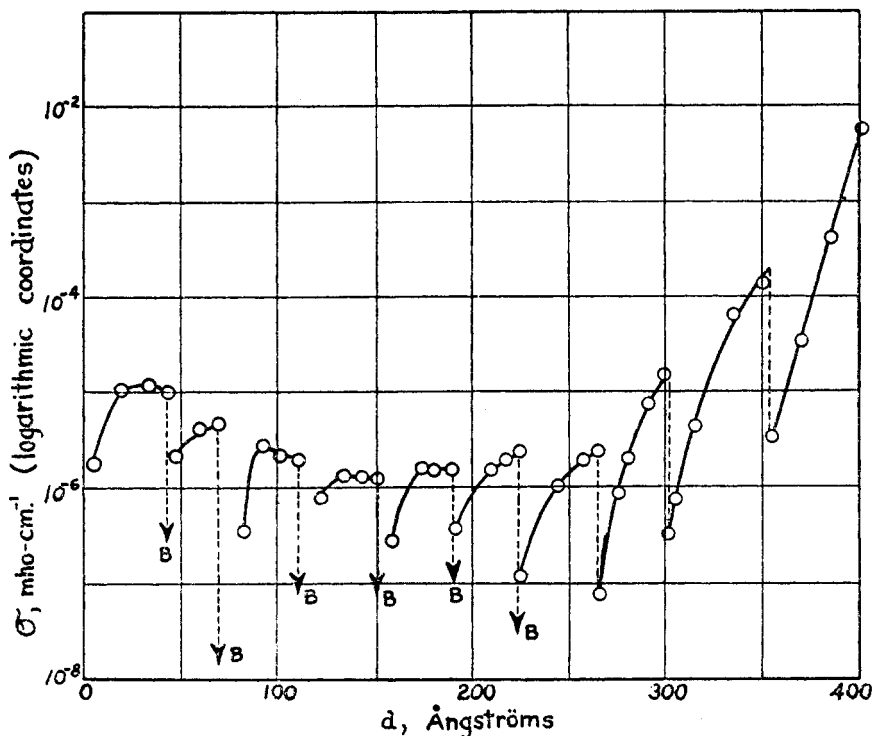


FIG. 4. Conductivity vs. statistical film thickness at 290°abs. for interrupted film formation at a deposit rate of 7.5 Å. per minute. B indicates complete disappearance of film conductivity (background). This disappearance continues until approximately 230 Å. are reached.

The rate of disappearance is better followed for films formed at low temperature, i.e., between 20° and 40°abs. (figure 6), and subsequently exposed to a variety of higher temperatures. It appears that this trend controls the behavior of films regardless of whether they were formed at high or low temperature.

(b) At temperatures of original formation and subsequent exposure below 50–100°abs. down to 14°abs., the films show a tendency opposite to the above, inasmuch as the conductivity increases under proper conditions rapidly over a remarkably large order of magnitude. For instance, in figure 7 (curves I and

II) the resistance was found to decrease by a factor of about 5000 within 75 min. after exposure. This behavior is only observable if, as a paramount condition, contamination by gas condensation on the surface is avoided, since the metallic properties of films of this type are exceedingly sensitive to any sort of surface disturbance, which always acts destructively upon conductivity.

Trend (b) is definitely temperature dependent, as evident particularly from curves I and II in figure 7, where the rate increased substantially when the film

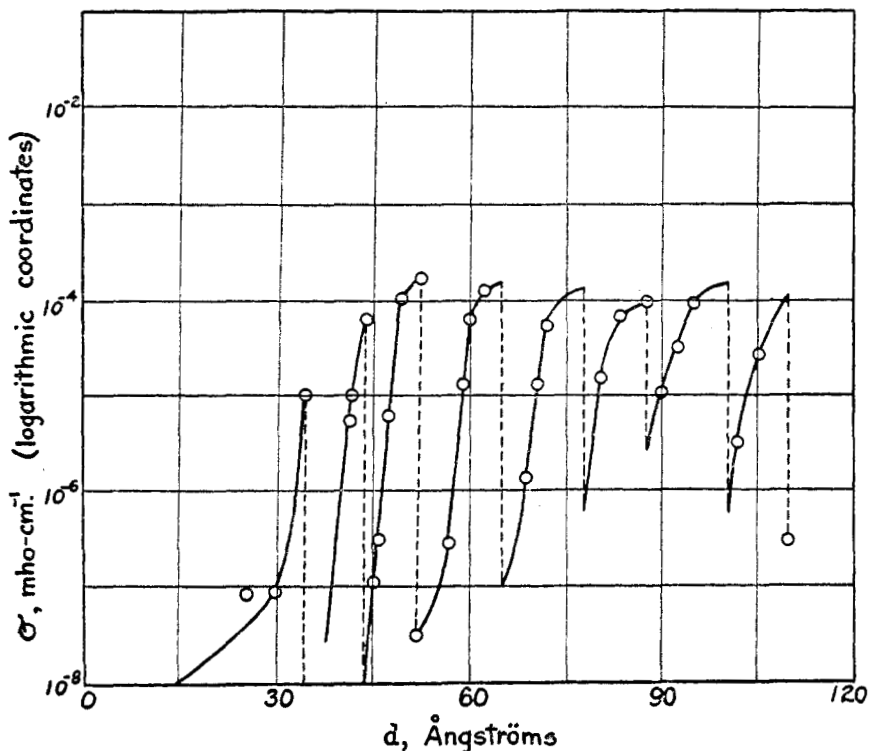


FIG. 5. Conductivity vs. statistical film thickness at 90° abs. for interrupted film formation at a deposit rate of 2 Å. per minute. Complete disappearance is only observed up to 50 Å.

was heated from 14° abs. to 90° abs. or respectively from 20° abs. to 50° abs. and then from 50° abs. to 90° abs.

The transition from the temperature range in which the two opposing tendencies prevail is not sudden, but extends over an interval in which both may even balance each other so that a certain stability may be apparent. This transition temperature depends obviously upon the number of atoms contained in the film in the sense that fewer atoms seem to expose trend (a) already at lower temperature, provided the latter is above 90° abs. The reverse appears to be true for tendency (b): for slightly thicker films trend a can prevail above 90° abs.

It is also significant that a deposit formed in the range (a) will not show the tendency (b), if rapidly cooled after deposit; in other words, the tendency (b) has been observed only in layers formed at a low temperature.

This observation does not hold for films formed at low temperature and subsequently exposed to the trend *a* for a time interval insufficient for complete destruction of conductivity. In this respect curve I in figure 6 may serve as an example. Exposure to 110°abs. for 10 min. shows trend (a), and subsequent exposure to 65°abs. trend (b); heating for about 10 min. to 140°abs. alters the trend again and strongly to (a), while subsequent cooling to 90°abs. and 65°abs. re-

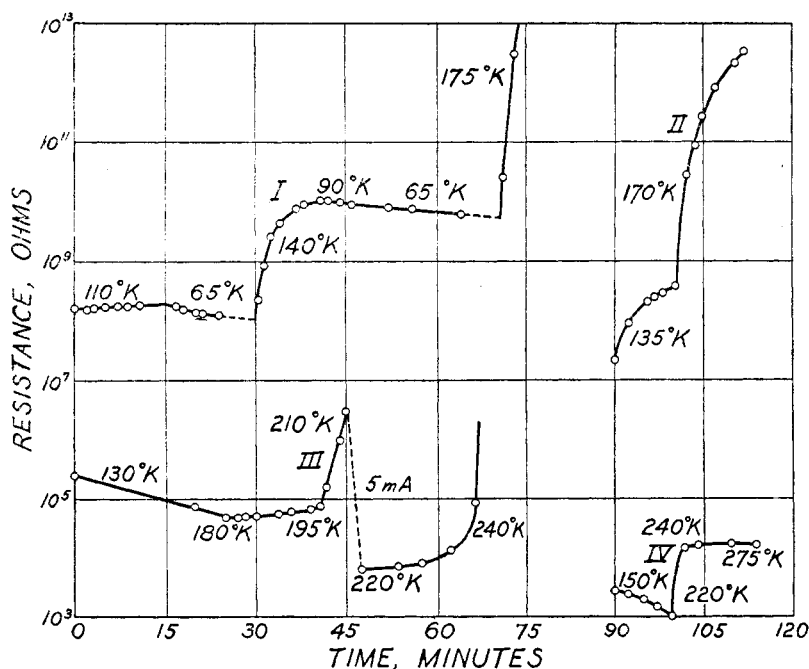


FIG. 6. Time-resistance variation after exposure to temperatures above 90°abs. The temperatures after exposure are practically all within the realm of trend (a) (resistance increases with time).

verses the trend to (b), until final heating to 175°abs. destroys the conductivity irreversibly.

A substantially heavier film (curve III) at 130°abs. still shows trend (b), and heating to 180°abs. is required to produce a (not very large) reversal.⁴

This complex behavior indicates, obviously, the existence of two mutually contradictory stabilities of configuration, of which one (tendency *a*) is obvious

⁴Though not the subject of specific discussion in this presentation, it may be mentioned that in the case of film III a current of 5 milliamperes was passed through from a separate source for about 3 min.; this decreased the resistance by a factor of about 90 without destroying the sensitivity of the film to trend (b).

from thermodynamic considerations and has been reported by numerous observers (1, 2, 8, 10, 11, 14): the thermodynamic potential of the deposit of a few statistically arranged atomic layers produces the tendency for a configuration exposing lesser surface and containing, at least over limited realms, a higher degree of order (partial lattice formation). This more stable configuration will be one of globules (droplets) of semicrystalline character.

This type of configuration will render a coherence of the film, even in the sense of a few bridges, improbable as long as the original deposit contained a relatively

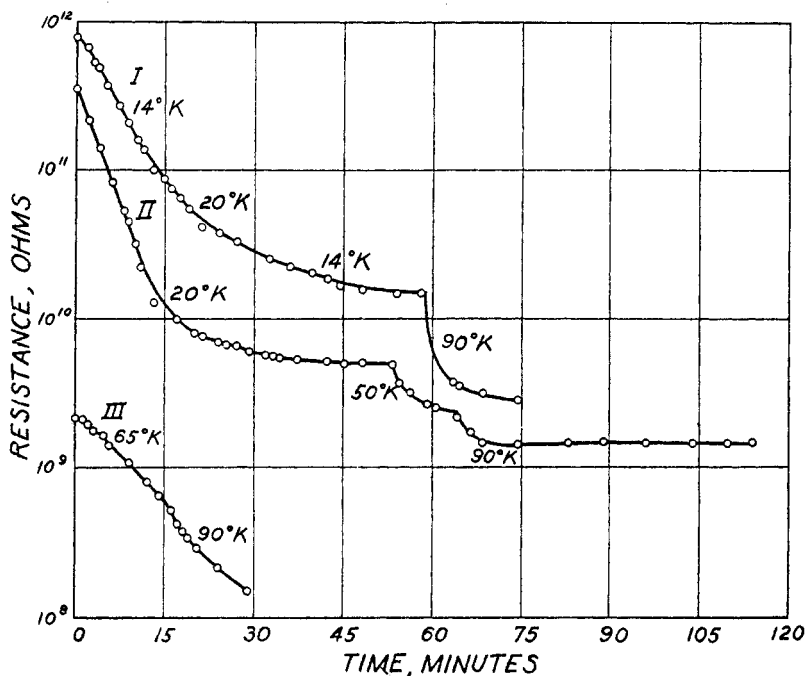


FIG. 7. Time-resistance variation after exposure to temperatures below 90°abs . The temperatures after exposure are all within the realm of trend (b) (resistance decreases with time).

small number of atoms. This lack of coherence is manifested in the disappearance of the conductivity.

The rate at which this transition occurs from a statistically arranged condensate into the semicrystalline globule depends obviously on the mobility of the molecules on the surface, and it appears remarkable that at temperatures of approximately 170°abs the mobility of the lead atoms is still so large as to cause a disappearance of conductivity at the rate indicated in figure 6 (curves I and II).

It should, however, not be overlooked that this tendency, based upon a high mobility of lead atoms at fairly low temperatures, can only exist if it compensates sufficiently the surface forces which produce adsorption, which should have

the tendency to "spread" the molecules of a deposited layer into a configuration of fairly uniform occupancy of the surface (as long as the number of molecules is sufficiently small to be still subject to the surface forces). The cause for this apparent inactivity of the surfaces may be that, in spite of all efforts to outgas the condensation surface previously, adsorption of sufficiently available residual gas molecules at low temperature has already annihilated the surface activity (saturation of the van der Waals forces), so that the condensation of the lead molecules occurs on a "compensated" surface.

The cause of trend (b) is less obvious than of (a); the experiments show that it is only observed on films formed at low temperature, i.e., for layers which during formation have not been subject to trend (a). The phenomenon must thus be associated only with molecular configurations which have not yet been transferred into the quasi-crystalline state of isolated globules. Neither can trend (b) be interpreted by the absence or restriction of molecular mobility at sufficiently low temperatures and a consequent inability to coalesce, since definite changes do occur after exposure to the beam. In other words, if only absence of coalescence were the cause, a definite conductivity should be associated with a definite number of molecules in the film and no further change after the exposure should be expected.

Several observers (3, 6, 7, 9, 14, 15) have also reported an increase in conductivity, but a definite distinction between the behavior during and after film formation at low temperatures is in general not made. This distinction appears to be of particular importance in view of an interpretation of this trend. Two different types of reaction causing it can be offered,—one based purely on the geometry of the configuration, the other on intermolecular changes.

The former must postulate that, instead of the high-temperature tendency to form a configuration of isolated globules which disrupt the film continuity, at low temperatures a different type of (thread-like) structure prevails, the formation of which assists the establishment of conductive bridges. The probability of this interpretation appears restricted.

The other type of explanation must assume the existence of a molecular film configuration for low-temperature deposits which possesses, in spite of physical coherence, either no or only restricted metallic qualities. One possibly not too far fetched hypothesis would be this: condensation from the molecular beam at sufficiently low temperature results in a statistical surface deposit wherein the molecules are still in the non-metallic state in which they existed in the vapor phase of the beam. The individual molecules are separated from each other by potential barriers which cannot be overcome because of lack of thermal energy available under the conditions of closely isothermal low-temperature condensation (conditions (a)–(c); see above). Since, however, the activation potential required for the intermolecular transition into the conductive phase is probably very small, even a temperature of 14°abs. (which is probably much higher locally at the instant of molecular impact) may not be low enough to avoid this transition completely, and the majority of the (very slowly) deposited molecules will require a considerable amount of time for this transition. Trend (b) would

thus be caused by a gradual transition from a non-metallic into a metallic state by the establishment of an electron configuration within the film, apparent by a gradual increase in conductivity. This finally completely established state is maintained as long as the film temperatures remain sufficiently low to prevent significance of trend (a), i.e., coalescence.

The suggestion of a transition from an amorphous non-metallic into a crystalline metallic phase was first made by J. Kramer (3, 6, 7, 15) and his school and was based upon his observation of sharply defined transition temperatures of the type known for allotropic transformations. Several other investigators have not been able to confirm the general validity of this assumption; it is obviously incorrect for our observations of lead. At the same time they demonstrate, however, that if lesser precautions for the control of the film temperature during and after exposure had been taken, a sharp instead of a gradual transition into the conductive state could easily have been recorded, in view of the large temperature dependence of trend (b) (e.g., curve I in figure 7). There is little doubt that this interpretation is correct for certain elements of lesser metallic character of which non-metallic "amorphous" modifications are known to occur already at room temperature, e.g., antimony and arsenic.⁵

A not dissimilar interpretation of the nature of trend *b* has been suggested by Suhrmann and his collaborators (13): the increase in conductivity at low temperatures is due to a transition from a state of lesser to one of higher order of molecular configuration, the latter being the better conductor. An activation energy of the order of 150–800 cal. per gram-atom, characteristic for each metal, is required for this transition. Obviously this type of statistical transition does not require a defined transformation point and differs thus from Kramer's assumption.

Suhrmann's hypothesis is analogous to the one suggested in this paper, but differs in the apparent assumption of metallic properties for the original film deposit in the state of low order. However, it seems difficult to account for the magnitude of the conductivity changes observed under these conditions solely with a transition from a disordered to an ordered state.

Since films which show this behavior are exceedingly delicate and unusually sensitive to external disturbances, attempts to study this state by electron diffraction may prove futile. On the other hand, it is hoped that adequate

⁵In spite of the absence of a defined transition temperature, it is not excluded that for the case of lead a true α -modification of non-metallic character and stable only at very low temperature exists in the film at these particular conditions of condensation and that the increase of conductivity would be caused by a gradual transformation into the β -modification, so far known only for lead. The transformation rate could safely be assumed to be very low, if the transformation point should lie somewhat above 14° abs. This would be a very close analogy to the existence and behavior of the α - and β -modifications of tin, the vertical neighbor of lead in the fourth column of the Periodic System. The other elements of this column—with the probable exception of silicon—show the same type of allotropy: a non-conducting form unstable at high temperature, and a β -form with at least semimetallic properties, well known for carbon (diamond-graphite) and recently established for germanium by Koenig (5).

techniques can be developed to form and observe such films at helium temperatures, particularly with regard to the occurrence of superconductivity. If, according to the above (and also Kramer's) suggestion, the low-temperature film consists of mutually isolated lead molecules and is thus essentially non-metallic in character, it should, even for considerable thickness, not become superconductive, for the same reason that, in contradistinction to β -tin, α -tin is not a superconductor. If, according to Suhrmann, the molecular properties are already metallic but the array one of disorder, it may be expected that for sufficiently low temperatures superconductivity will be observed.

REFERENCES

- (1) ANDRADE, E. N. DA C., AND MARTINDALE, J. G.: *Phil. Trans. Roy. Soc.* **235**, 69 (1935).
- (2) BRAUNBEK, W.: *Z. Physik* **59**, 191 (1930).
- (3) CELEBI, M.: *Z. Physik* **106**, 702 (1937).
- (4) GOETZ, A.: *Z. Physik* **42**, 328 (1927).
- (5) KOENIG, H.: *Reichsber. Physik* **1**, 4 (1943).
- (6) KRAMER, J.: *Ann. Physik* **19**, 37 (1934).
- (7) KRAMER, J.: *Z. Physik* **106**, 675, 692 (1937).
- (8) LOVELL, A. B. C.: *Proc. Roy. Soc. (London)* **157**, 311 (1936).
- (9) MITCHELL, A. C. G.: *Phys. Rev.* **53**, 250 (1938).
- (10) SUHRMANN, R., AND BARTH, G.: *Physik. Z.* **35**, 971 (1934).
- (11) SUHRMANN, R., AND BARTH, G.: *Z. Physik* **103**, 133 (1936).
- (12) SUHRMANN, R., AND BERNDT, W.: *Physik. Z.* **37**, 146 (1936).
- (13) SUHRMANN, R., AND SCHNACKENBURG, F.: *Z. Elektrochem.* **47**, 277 (1941).
- (14) WAS, D. A.: *Physica* **4**, 382 (1939).
- (15) ZAHN, H., AND KRAMER, J.: *Z. Physik* **86**, 413 (1933).