AIP Journal of Applied Physics

Conducting Thin Films Formed by Electron Bombardment of Substrate

R. W. Christy

Citation: Journal of Applied Physics **33**, 1884 (1962); doi: 10.1063/1.1728851
View online: http://dx.doi.org/10.1063/1.1728851
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/33/5?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS VOLUME 33, NUMBER 5 MAY, 1962

Conducting Thin Films Formed by Electron Bombardment of Substrate*

R. W. CHRISTY†
Space Technology Laboratories, Inc., Los Angeles 45, California

(Received October 31, 1961)

A new technique for depositing thin films has been investigated. The method consists in decomposing molecules on a substrate by bombarding them with electrons, leaving metal atoms on the substrate. The film is formed selectively on the area of the substrate struck by the electrons. Stannous chloride was decomposed to metallic tin by electrons of about 200 ev energy .Tetrabutyltin was also studied. With the current densities available, tetrabutyltin was only partially decomposed, to form a semiconducting polymer film. Theoretical considerations suggest that the method should be applicable to a wide variety of metals.

I. INTRODUCTION

THE usual methods for producing thin conducting films on an insulating substrate are vacuum evaporation, sputtering, and vapor plating. We have investigated a new method, which consists in continually decomposing on the substrate molecules containing the substance to be deposited, the decomposition being effected by an electron beam, or other ionizing radiation. The molecules adsorbed on the surface, on excitation by an electron impact, dissociate into a metallic component which remains on the substrate and a volatile component which leaves, so that a metallic film is progressively built up. The process is most closely related to vapor plating,[1] where molecules are thermally decomposed on contacting a hot substrate, so that the refractory metal component remains on the substrate. The present method of decomposition offers an advantage over vapor plating where a certain configuration of the conducting film is wanted, since the areas bombarded can be controlled by forming an electron image or by scanning with an electron beam. In this respect it also promises an advantage over evaporation through a mask, in reduction of penumbra, and in the demagnification achievable. In addition, it can be applied to metals which would vaporize or melt on a hot substrate. In certain applications, ultraviolet light or other radiation might be preferred to electrons. The method is also closely related to the formation of thin insulating films by electron bombardment of the substrate in the presence of an organic vapor.[2–5]

II. THEORETICAL CONSIDERATIONS

The mechanism of the film formation differs from the one responsible for vapor plating in a significant respect. Thermal dissociation in vapor plating occurs when the vibrational energy in the ground electronic state of the molecule is increased to the point where it is greater than the potential energy of binding. In the present process, on the other hand, the molecule is excited by the electron impact to a higher electronic state, which, in the simplest case at least, is an unbound state, so that the molecule flies apart without the requirement of any thermal energy.[6] Thus there is not necessarily any direct relation between the thermal instability of a molecule (in the ground electronic state) and the probability that it will dissociate under irradiation (from an excited state). Figure 1 shows typical energy level diagrams which would lead to dissociation on excitation.

The dissociation from the excited state will occur in the same way, no matter whether the excitation was originally produced by an electron or photon, though, of course, the transition probabilities to the various excited states of the molecule depend on the nature and the energy of the exciting radiation. Excitation and dissociation of molecules have been extensively studied, mainly in the vapor but also in condensed phases. These investigations belong primarily to the fields of molecular spectroscopy,[7] photochemistry,[8] mass spectrometry,[9,10] and nuclear chemistry.[11] The accumulated information affords a general understanding of the effects to be expected in forming thin films by decomposition, although there are some features of the dissociation of a molecule on the surface of a solid which would not be anticipated.

The excitation of molecules by electron impact occurs with a total cross section[10] roughly equal to the geo-

---

* This work was supported in part by the General Research Provision of contract between the Air Force and Space Technology Laboratories, Inc., and in part by the Office of Naval Research.

† Permanent address: Department of Physics, Dartmouth College, Hanover, New Hampshire.

[1] C. F. Powell, I. E. Campbell, and B. W. Gonser, *Vapor Plating* (John Wiley & Sons, Inc., New York, 1955).

[2] R. Haefer, *Proceedings of the 3rd International Conference on Electron Microscopy, London, 1954* (The Royal Microscopical Society, London, 1956), p. 466.

[3] K. R. Shoulders, Stanford Research Institute Report "Research in Microelectronics Using Electron-Beam-Activated Machining Techniques," September 1960.

[4] R. W. Christy, J. Appl. Phys. **31**, 1680 (1960).

[5] After this paper was written, the author learned about a report of similar experiments by A. G. Baker and W. C. Morris [Rev. Sci. Instr. **32**, 458 (1961)].

[6] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), pp. 217-29.

[7] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (John Wiley & Sons, Inc., New York, 1947).

[8] G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions* (Prentice–Hall, Inc., Englewood Cliffs, New Jersey, 1939).

[9] A. Henglein, Angew. Chem. **71**, 393 (1959).

[10] See reference 6, Chap. IV.

[11] M. Haïssinsky, *La Chimie Nucléaire* (Masson et cie, Paris, 1957).

metrical cross section at low electron energies, of the order of 100 ev. Thus the probability for dissociation will be appreciable, unless there are tightly-bound excited states competing with those from which dissociation can occur. The excited states are known for a number of diatomic molecules. For poly-atomic molecules, the situation is more complicated, but there dissociation is often favored because of the greater complexity of the electronic states and normal modes of vibration.[12] The experimental evidence for dissociation by electron impact comes mainly from mass spectrometer studies, and therefore refers only to ionized fragments, since neutral free radicals would not be detected. There is evidence, however, that excitation, as well as ionization, plays an important role in dissociation,[13] as would be expected.

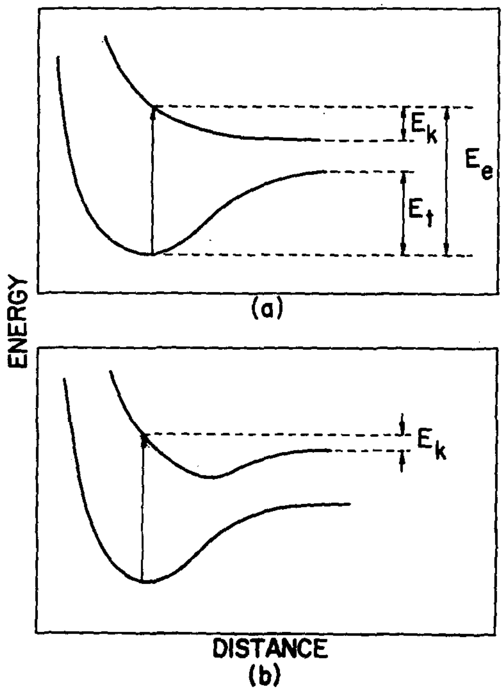

FIG. 1. Energy of a molecule as a function of a configuration coordinate (e.g., internuclear distance in a diatomic molecule). (a) The lower curve is the ground state, E_t being the thermal dissociation energy or the vibrational energy needed for dissociation. If the molecule is raised to the unbound-excited state (upper curve) by the absorption of E_e, the nuclei fly apart with kinetic energy E_k. (b) Dissociation may also occur when the excited state is a bound state. By the Franck–Condon principle the nuclear coordinates are unchanged during the excitation, so that the excited molecule may be left in a high enough vibrational state for dissociation to occur.

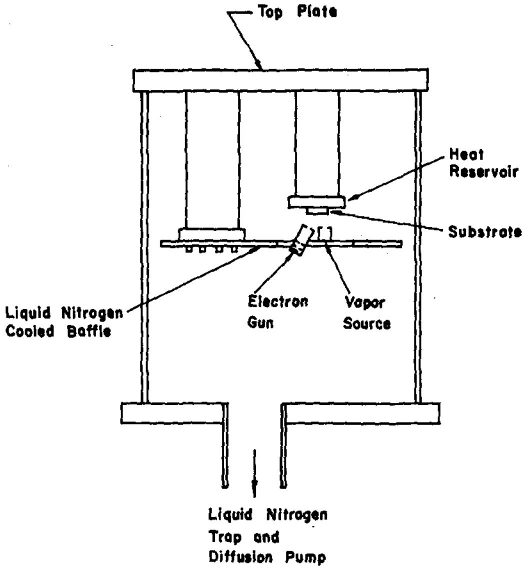

FIG. 2. Vacuum system in which films were produced.

Our attention has initially been directed principally toward tin and lead compounds, because of the superconducting properties of those elements. Stannous chloride $SnCl_2$, an ionic compound, and tetrabutyltin $Sn(C_4H_9)_4$, in which the bonds are covalent, have been studied in greatest detail. There appears to be no reason why the method could not be applied to the production of films of any other metal or semiconductor, however. In many applications, especially when sweeping the electron beam, it would be advantageous to decompose a compound which is more volatile than the metal, so that nothing remains on the substrate in areas which are not struck by the electrons. In this case organometallic compounds would be particularly interesting. These are also known throughout the periodic table.[14,15]

A phenomenological theory of the factors which influence the film growth rate has been discussed for polymer films,[4] and similar considerations can also be applied to the case of metallic films.[16]

III. EXPERIMENTAL RESULTS

The experimental decompositions were carried out in a bell-jar vacuum system. The substrate on which the film was formed was, in most cases, a polished quartz disk, mounted on a heat reservoir, whose temperature could be maintained either above or below room temperature. About 2 cm below the substrate were positioned a source of the vapor to be decomposed and an electron gun to provide the electron beam which effected the decomposition, as shown in Fig. 2. These were surrounded by a liquid nitrogen cooled baffle, intended to reduce the pressure of back-streaming diffusion pump oil or other organic vapors. The pressure in the system was of the order of 2×10^{-7} mm Hg, and under these conditions, without the vapor source, polymer film formation[4] proceeded at a negligible rate.

---

[12] See reference 8, pp. 74–6.

[13] R. R. Williams, Jr., J. Phys. Chem. **63**, 776 (1959).

[14] E. Krause and A. von Grosse, *Die Chemie der Metallorganischen Verbindungen* (Borntraeger, Berlin, 1937).

[15] E. G. Rochow, D. T. Hurd, and R. N. Lewis, *Chemistry of Organometallic Compounds* (John Wiley & Sons, Inc., New York, 1957).

[16] R. W. Christy, Space Technology Laboratories Report No. STL/TR-60-0000-NR 376, November 1960.

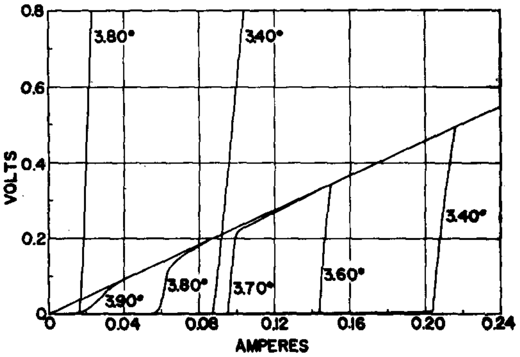

FIG. 3. Superconducting transition observed in tin film deposited on substrate at −60°C. The steeper curves show the initial portion of the transition for 3.80° and 3.40° on an expanded voltage scale ($10^4\times$).

The electron gun was a homemade triode, which provided an essentially uniform current density of 1 ma/cm^2 or less, over a spot of about 2 mm diameter. The accelerating voltage was 225 v. The vapor source was a copper cylinder, $\frac{1}{2}$ in. in diameter and $\frac{1}{2}$ in. high with 3/32-in. wall, and with a $\frac{1}{8}$-in. hole in the top. This source approximated an isothermal enclosure with a small hole. Its temperature could be regulated by a Nichrome heater wound on the outside of the cylinder. For source temperatures below room temperature, the source was mounted on a bracket attached to the liquid nitrogen reservoir.

Because the films were formed on a nonconducting substrate, the electron beam current could not be measured during the decomposition. It was, however, estimated on the basis of measurements made beforehand, as described previously.[4] The flux of molecules from the vapor source was calculated from the measured loss of weight of the vapor source, and the flux at the substrate was calculated from geometry; the flux could be controlled by adjusting the source temperature. These estimates are rather crude, but the values quoted are believed to be correct within about 50%.

The properties of the resulting films were determined by visual inspection, by treating them with solvents, by measuring their thickness,[17] and by measuring their electrical resistance. For the latter purpose, evaporated Pb electrodes were applied to either side of the spot. (Pb was used so that a superconducting transition could be observed.) No structural determinations or chemical analyses have yet been performed.

The results for the compounds which have so far been studied are as follows:

A. Stannous Chloride

Anhydrous stannous chloride $SnCl_2$ (Metal and Thermit Corporation, Rahway, New Jersey) is an ionic solid with boiling point 623°C. Metallic tin films were formed with a $SnCl_2$ evaporation rate in the neighborhood of 10^{-4} g/min at a source temperature of 190°C, corresponding to a flux at the substrate of $F=0.02$ molecule/Å^2/sec. (This flux would correspond to an equilibrium $SnCl_2$ vapor pressure of about 2×10^{-6} mm Hg, at a temperature of 130°C, assuming the coefficient of accommodation to be 1.) The electron flux was of the order of $f=0.1$ electrons/Å^2/sec. The rate of film formation under these conditions was of the order of 0.5 Å/sec.

The rate of film formation was independent of substrate temperature in the range of substrate temperatures from −90° to +30°C. It was approximately proportional to the vapor flux F between 0.005 and 0.05 molecules/Å^2/sec with the substrate at room temperature. Below −90° the films did not form well, perhaps because Cl_2 (mp −100°C) remained on the substrate.

The films which were produced on room temperature substrates were shiny when they were 500 Å thick, but rather rough when 1000 Å thick. The films produced at −60°C were shiny at 1000 Å thickness, although full of pinholes. For the latter films, the electrical conductivity and the critical current for the superconducting-to-normal transition were approximately one-third those for high quality evaporated tin films. The current-voltage characteristics are shown in Fig. 3. The films produced at room temperature had a smaller conductivity and critical current than those produced at −60°C.

The mechanism for the decomposition of $SnCl_2$ could be either

$$SnCl_2 \rightarrow Sn + Cl_2 \tag{1}$$

or

$$SnCl_2 \rightarrow SnCl + Cl\cdot, \quad SnCl \rightarrow Sn + Cl. \tag{2}$$

Photodissociation of $SnCl_2$ to SnCl has been observed;[18] the direct dissociation to $Sn+Cl_2$ was thought to be unlikely, although there was some evidence that it may have occurred. The absorption spectrum of SnCl shows a continuous absorption which indicates a dissociation reaction.[19] In the decomposition of ethane by 1-Mev electrons,[20] on the other hand, it seems that about half of the H_2 is formed by direct detachment of molecular H_2, without the apparent formation of atomic H. In the dissociation of $C\,Cl_4$,[21] $SiCl_4$,[22] and $SbCl_3$[23] by low energy electrons, however, the abstraction of Cl^- is very probable. Thus both reactions (1) and (2) should probably be considered.

The temperature dependence of the film growth rate comes from the temperature dependence of the mean time of stay of the molecules on the substrate—that is, how long they wait for a dissociating electron impact

---

[17] S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).

[18] H. Neujmin, Acta Physicochim. U.R.S.S. **2**, 595 (1935).

[19] C. A. Fowler, Jr., Phys. Rev. **62**, 141 (1942).

[20] L. M. Dorfman, J. Phys. Chem. **60**, 826 (1956).

[21] R. F. Baker and J. T. Tate, Phys. Rev. **53**, 683 (1938).

[22] R. H. Vought, Phys. Rev. **71**, 93 (1947).

[23] P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. **52**, 840 (1937).

before spontaneously evaporating from the substrate. The $SnCl_2$ molecules presumably wait a long time on a substrate at or below room temperature, since at room temperature the vapor pressure of $SnCl_2$ is very small. Thus the fact that the rate of Sn film growth is independent of temperature could mean one of two things: Either reaction (1) is the dominant reaction, or else the mean time of stay of SnCl molecules is also very long if reaction (2) contributes appreciably.[16] In either case, the rate of growth should be proportional to F, the rate of arrival of $SnCl_2$ molecules. In the second case, the tin film growth rate should be equal to vF, where $v=27$ Å^3 is the volume of a tin atom, and in the first case it should be nearly this large. The measured growth rate was in fact about $\frac{2}{3}$ of vF, but the measurements were not really accurate enough to discriminate between the two cases.

Since metallic tin films were obtained for ratios of electron flux to molecule flux as small as $f/F=2$, the cross section for the decomposition is apparently large. This fact may argue for the more efficient removal of Cl described by reaction (1).

In these experiments, areas of the substrate not struck by the electron beam were covered with a film of $SnCl_2$. This could be rinsed off with water afterwards, but it would be interesting to consider the decomposition of $SnCl_4$, which is a volatile liquid at room temperature. Since $SnCl_4$ tends to decompose to $SnCl_2$, the dissociation of $SnCl_2$ studied here would probably be rate-controlling.

When an already existing $SnCl_2$ film (about 3000 Å thick) was bombarded with the electron beam, a faint spot appeared after a few minutes, and then no further changes occurred during the 30 min of bombardment. Presumably in this case, the $SnCl_2$ was decomposed to a depth of the order of 100 Å, since the low energy electrons could penetrate no deeper.

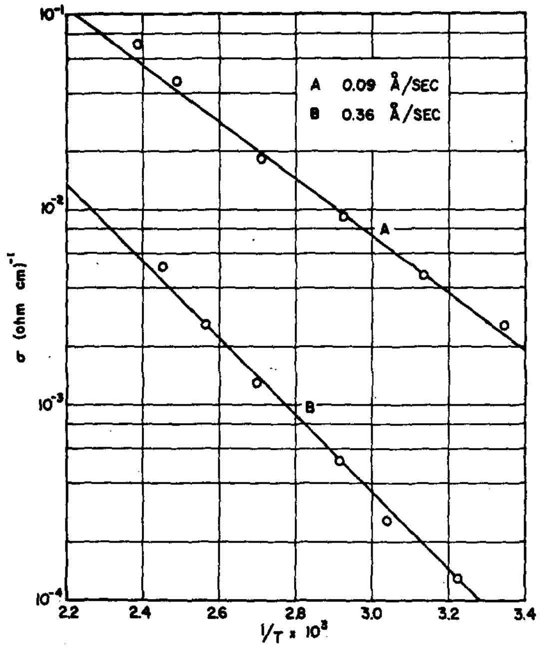

FIG. 4. Temperature dependence of conductivity for polybutyltin films.

B. Tetrabutyltin

Tetrabutyltin $Sn(C_4H_9)_4$ (Metal and Thermit Corporation, Rahway, New Jersey) is an organometallic liquid with boiling point 145°C at 10 mm Hg. This compound was decomposed under conditions similar to $SnCl_2$, that is to give a flux at the substrate of $F\approx 0.02$ molecules/Å^2/sec, with an evaporation rate of about 2×10^{-4} g/min from the source at 25°C (corresponding to an equilibrium vapor pressure of the order of 2×10^{-6} mm Hg at -30°C). Electron beam current densities to give an electron flux $f\approx 0.1$ electrons/Å^2/sec were used.

In contrast to the results with $SnCl_2$, metallic tin films were not formed under these conditions, but a semiconducting polybutyltin polymer film was produced. This phenomenon is more complex, in that both the growth rate and the composition of the film are dependent on current density, substrate temperature, and the flux of molecules. For many of the films, formed on a polished copper substrate, the thickness was not measured, so the rate of formation is not known. What was observed was the integrated flux of molecules (product of F and the total deposition time) required to produce a strongly absorbing film. Since the optical absorption depends on both the thickness of the film and its composition (i.e., the ratio of the number of organic radicals to the number of tin atoms in the polymer film), this integrated flux is a function of both properties.

The composition of the film depends on the molecule flux F, since with $F=0.02$/Å^2/sec an absorbing film was produced at an integrated flux of 30/Å^2, whereas when $F=0.2$/Å^2/sec the film was still transparent (absorption about 10× smaller) at 150/Å^2. In both cases the electron flux f was about 0.2/Å^2/sec and the substrate temperature was 25°C. Since the second film must have been thicker and yet was less absorbing, this film produced at a higher molecule flux contained more organic radicals.

As a function of substrate temperature, with $F=0.02$/Å^2/sec, $f=0.2$/Å^2/sec, the integrated flux required to form a strongly absorbing film was about 5× greater when the substrate temperature was 70°C, and about 5× smaller when it was -10°C. At substrate temperatures below -20°C, the situation changes. Here films formed with $f/F\approx 1$ were partially soluble in benzene, whereas when formed at the higher temperatures they were tough and insoluble. These changes represent variations in both the rate of formation and the composition.

The films produced at substrate temperatures above -20°C were insoluble in acetone, benzene, and aqua regia, and could be removed from the substrate only by fairly vigorous rubbing. They could be heated to 150°C in air, without apparent change. The material was semiconducting, as shown in Fig. 4. (Sample A was 900 Å thick, sample B, 3200 Å.) These films were formed on substrates near 25°C, $f \approx 0.1/\text{Å}^2/\text{sec}$, with different values of molecule flux F. The film formed at the higher rate showed an activation energy of 0.4 ev and at the lower rate 0.3 ev, again demonstrating that F affects the composition. The electrical conductivity is comparable with intrinsic germanium. The conductivity of the films progressively underwent a permanent increase on annealing in vacuum at 150°C, increasing by a factor of 2 in about 2 hr.

The temperature dependence of the rate of formation and the composition arises through the temperature dependent mean time of stay of the molecules on the substrate τ. At low temperatures the molecules wait until they are hit by an electron, the rate of film formation is equal to the rate F of arrival of the molecules, and the composition (number of bonds broken, with the removal of a butyl radical) depends on the ratio f/F; both rate and composition are independent of τ. When $f/F \approx 1$, the number of cross links formed (about one per molecule) is too small to give an insoluble film. As the temperature is increased and τ decreases, the rate of formation decreases because some molecules escape before being struck by an electron and the rate depends on electron flux f as well as the molecule flux F. In addition, the probability for a given molecule to be hit several times before being covered up is higher, so that the proportion of butyl radicals incorporated into the film decreases. For a given composition, the rate of formation is proportional only to electron flux f and the cross section for the reaction. This cross section is apparently only a few percent of the geometrical cross section.[16]

The difficulty of completely decomposing tetrabutyltin was surprising, since the similar tetramethyl lead $Pb(CH_3)_4$ is readily photylized by uv light,[24] with an over-all quantum efficiency of 1.1 in the vapor and 0.4 in solution. The principal over-all reaction was

$$Pb(CH_3)_4 \rightarrow Pb + 2C_2H_6,$$

but free methyl radicals CH_3 were detected. According to Clouston and Cook,[25] the primary reaction is

$$Pb(CH_3)_4 \rightarrow Pb(CH_3)_3 + CH_3$$

with subsequent decomposition of the unstable $Pb\,(CH_3)_3$. They also found CH_4, C_2H_4 and C_2H_2. Tetraethyl lead,[24–26] tetraphenyl lead,[24] and tetramethyltin[25] are also decomposed, but less efficiently. Films of solid tetramethyl lead about 0.1 mm thick have been decomposed[27] by x rays at 4°K, with the production of CH_4; on warming to 40°K, they turned opaque because of formation of free Pb.

Probably the difficulty in the present case arises partly because of stability of the $Sn—(C_4H_9)$ bond. A more important effect, however, may be that when a (C_4H_9) radical is detached, it abstracts an H atom from another (C_4H_9) radical still attached to a neighboring Sn atom,[28] with the formation of a $Sn—(C_4H_8)—Sn$ linkage. It would presumably then be more difficult to remove this radical tied to two Sn atoms. If the flux of electrons were increased relative to the flux of molecules, until the point was reached where an arriving $Sn(C_4H_9)_4$ molecule was unlikely to be next to any other butyl radicals, complete decomposition should occur.

IV. CONCLUSIONS

It has been demonstrated that metallic thin films can be produced on a substrate selectively in areas struck by an electron beam. The films showed a distinct superconducting transition. The deposition rate obtained was rather small, less than 1 Å/sec, but it can be increased. The rate was limited by the electron current density, which could probably be increased by a factor of 10^3 at 100-v anode voltage,[29] and more at higher voltages. This would give deposition rates comparable with those presently obtainable by evaporation. The molecule decomposed, $SnCl_2$, is typical of compounds throughout the periodic table, so that the process should be applicable to a wide variety of metals.

Especially in applications where the film is formed by scanning with an electron beam, it would be preferable to decompose a volatile compound. (Otherwise, the sweep rate would have to be high enough for the electrons to penetrate the layer accumulated since the previous sweep.) In this respect, organometallic compounds suggest themselves. The decomposition of tetrabutyltin has pointed up an effect, the formation of a polymer film, which may be expected with the alkyl compounds of tetravalent, and possibly also other, metals. This effect apparently arises from the formation of an alkyl linkage between two metal atoms. It might be less with the methyl compounds, or with halogen-substituted compounds. It could not occur with the tetrahalide or tetrahydride. On the other hand, the semiconducting polymers produced, with a conductivity which is controllable by the electron beam intensity, may be very interesting in themselves.

ACKNOWLEDGMENTS

The low temperature conductivity measurements were made by Dr. A. J. Learn. The author also wishes to thank him and R. Spencer Spriggs for helpful discussions. We would like to thank the Metal and Thermit Corporation and E. I. du Pont de Nemours and Company for the gift of organometallics.

---

[24] P. A. Leighton and R. A. Mortensen, J. Am. Chem. Soc. **58**, 448 (1936).

[25] J. G. Clouston and C. L. Cook, Trans. Faraday Soc. **54**, 1001 (1958).

[26] A. Terenin and N. Prileshajewa, Acta Physicochim. U.R.S.S. **1**, 759 (1935).

[27] I. L. Mador. J. Chem. Phys. **22**, 1617 (1954).

[28] Cf., A. A. Miller, E. J. Lawton, and J. S. Balwit, J. Polymer Sci. **14**, 503 (1954).

[29] D. B. Langmuir, Proc. I.R.E. **25**, 977 (1937).