Early History of Vacuum Arc Deposition

Raymond L. Boxman, *Fellow, IEEE*

Invited Paper

***Abstract*—Vacuum arc deposition (VAD) was first investigated at the end of the 19th century by A. W. Wright and T. A. Edison, as mirror coatings and seed layers for phonogram replication molds, respectively. The early research anticipated later developments, including cathode shielding, multi-layer coatings, substrate motion, and hybrid processing.**

***Index Terms*—Coatings, Thomas A. Edison, history, thin films, vacuum arc, Arthur W. Wright.**

I. INTRODUCTION

THE VACUUM arc is a high current electrical discharge in which the electrical current is conducted in plasma consisting of ionized material emitted from the arc electrodes as a result of the discharge. This plasma condenses on any cool surface which it contacts, and thus may be used to fabricate thin films and coatings [1]. The first investigations of the vacuum arc, in the 19th century, were centered on this application. The details of the early investigations are generally not known by modern researchers and practitioners. The objective of this review is to acquaint present researchers with the early history of vacuum arc deposition (VAD).

II. A. W. WRIGHT

The earliest published investigation of VAD was conducted by Arthur W. Wright at Yale University, New Haven, CT. Wright was one of a batch of three students who were the first Americans to receive a Ph.D. degree in science in an American university from an American professor of science. Wright subsequently founded and directed the Sloane Physics Laboratory at Yale and, in 1966, the University's Nuclear Structures Laboratory was named for him.

The motivation for Wright's work was a desire to rid residual Hg vapor from glass vacuum tubes [2]. Wright's apparatus consisted of a pair of electrodes within a glass envelope, which were energized from a power supply consisting of a battery of Grove cells and an induction coil. While not stated explicitly, presumably the circuit was connected as shown in Fig. 1. Opening the switch while current is flowing imposes a high-voltage pulse across the discharge tube, causing breakdown and, subsequently, the current in the coil flows through the discharge. Presumably,

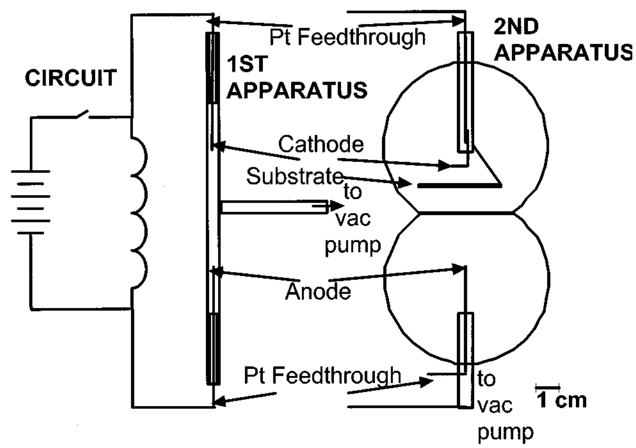

Fig. 1. A. W. Wright's apparatus. Rendition based on written text [2], [3].

the switch was repetitively operated to produce a series of pulses. The discharge electrodes were 0.25–0.5 mm diam wires.

Wright sought to deposit a thin Au film with a large surface area on the tube wall, which would amalgamate with the Hg vapor, and thus remove it from the tube volume. He observed that a thin film was deposited near the cathode. While deposition from the cathode is characteristic of the vacuum arc, it is likewise characteristic of sputter deposition in a glow discharge, and thus the question arises of whether the discharge was a glow or an arc. An oscillogram of the arc voltage would probably resolve the question, but of course this was unavailable at the time. It is likely, however, that the inductor current was sufficiently great and the cathode diameter sufficiently small, that the discharge operated in the arc mode.

When "a powerful discharge was maintained for a considerable time," a "slight deposit" was observed opposite the anode. This is perhaps the forbearer of deposition by the "hot anode vacuum arc."

In his initial studies, Wright deposited metal films on the walls of glass discharge tubes. The residual pressure in the tubes was about 1–2 torr. Wright prevented oxidation of his films by repetitively backfilling his chamber with H_2 and pumping. In a later study [3], Wright used a miniature glass deposition chamber, in which the substrate was suspended. By tilting his apparatus, the relative position of the source cathode and substrate could be adjusted, which allowed Wright to obtain more uniform coatings.

Wright commented on the visual appearance of the films produced, both by reflected and transmitted light (Table I). He noted that ~ 200 nm Au and Pt films had barely perceptible transmission, but very good reflection. The Pt films were recommended

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The author is with the Electrical Discharge and Plasma Laboratory, Fleischman Faculty of Engineering, Tel Aviv University, Tel Aviv 69978, Israel (e-mail: boxman@eng.tau.ac.il).
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TABLE I
OPTICAL PROPERTIES OF THIN METAL FILMS DEPOSITED BY WRIGHT, GROUPED BY EASE OF DEPOSITION

Material	Transmitted Color	Reflected Color	Luster
Bi	Blue-gray		Brilliant
Au	Pink-blue-green	Gold	Beautiful
Ag	Blue		
Pt	Gray, blue tinge		
Pd	Smokey brown		
Pb	Olive-smoky brown		Feeble
Sn	Brwn-gray, sepia		Poor
Zn	Deep grayish blue	Wt-silver	Brilliant
Cd	Deep grayish blue	Wt-silver	Brilliant
Cu	Dull green		Fine
Fe	Neutral (brwn tinge)		Brilliant
Ni			
Co			
Al	Brownish		
Mg	Grayish-blue		

for mirrors, due to their chemical stability. Wright found that Ag, Au, and Pt films remained adherent to their glass substrates even after two weeks immersion in water. Wright also deposited Pt/Ag/glass double layers, in order to compensate for the slight reflective color from each layer separately and to improve the chemical stability of the Ag layer. It was difficult to obtain Ni films without oxidation. However, the Fe coatings were surprisingly stable to moist air and nitric acid.

III. Thomas A. Edison

Thomas A. Edison, the most famous American inventor and industrialist of the late 19th century, filed a patent application in 1884 claiming "*..a process of plating one material with another by vaporizing the material to be deposited in a vacuum…*"; a "*…process of plating one material with another by electro-vacuous deposition*"; the "*process of plating with electrical conducing material by forming an electrical arc between electrodes of the material in a vacuum….*"; and the"*process of plating with an alloy or composition of electrical conducting materials, by forming an electric arc between electrodes of different metals in a vacuum…*" [4]. Edison was assisted in this research by a Mr. Schulze-Berge, who previously had been an assistant to Helmholtz [5]. A ten-year struggle with the U.S. Patent Office ensued. The patent examiners demanded that the vague term *electro-vacuous deposition* be defined [6], and pointed out the previous work by Wright [7], of which Edison was apparently unaware. Edison, in a modified application, described Wright's work as "*…merely a laboratory experiment and could not be practically applied because the formation of the deposit by the intermittent or alternating spark is too slow to be commercially useful. I have found that by using a continuous arc the process is made infinitely more rapid and certain…*". He was forced, however, to modify his fundamental claim to vacuum arc deposition, narrowing his claim to the use of a continuous electric arc. The patent was finally issued on September 18, 1894 [8].

In 1888, Edison filed an additional patent application for a process of duplicating phonograms (Fig. 2). His original phonograms were wax cylinders, onto which the sound track was mechanically impressed. Edison used a vacuum arc to coat the phonographic impression. Once a good initial deposition was built up, electrochemical deposition was used to increase its thickness. Finally, the wax substrate could be removed, leaving a free-standing cylindrical coating containing the inverse sound track impression on its interior surface, which served as a mold for casting additional phonograms [9].

IV. Achievements and Influence of the Vacuum Arc Pioneers

Wright's and Edison's work anticipated many later developments, including the use of a cathode shield to confine the discharge to a desired portion of the cathode, inductive energy storage, multilayer coatings, motion of the substrate to obtain a uniform deposition, the debate about the efficacy of pulsed versus continuous arc deposition and a hybrid process using physical vapor deposition to produce a seed layer and electrochemical deposition to deposit the main layer (as currently practiced for Cu metallization of ultra-large scale integrated circuits). However, this early work was mostly forgotten. L. Holland, a vacuum deposition pioneer, cited Edison's phonogram duplication patent in a letter to *Nature* in 1956 [10], and Kikuchi *et al.*, the first scientists to apply modern methods to the study of vacuum arc deposited films, cited Holland's letter [11]. However, no further mention of Edison's or Wright's work appeared, until cited at the 13th International Symposium on Discharges and Electrical Insulation in Vacuum [12], a century after Edison's first vacuum arc patent application. Just as Edison apparently rediscovered VAD, unaware of Wright's work, VAD was rediscovered by a long list of investigators (including the present), in blissful ignorance of the early pioneering work.

While various investigators suggested using VAD in the interim years and several patents were granted, the first modern investigations of the properties of vacuum arc coatings was conducted by Kikuchi *et al.* [11], and later by Naoe *et al.* [13] in Tokyo. Vacuum arc deposition was industrialized in modern times by a team in Kharkov including Aksenov *et al.*, leading to the *Bulat* series of deposition systems in the 1970's. Just as Wright's pioneering work grew out of a desire to improve vacuum conditions, this work grew from an earlier development of a Ti vacuum arc sorption pump [14]. VAD technology was brought to the West $\sim$ 1980 by a NY based precious metals dealer, J. Filner, who was shown the technology in the former U.S.S.R.

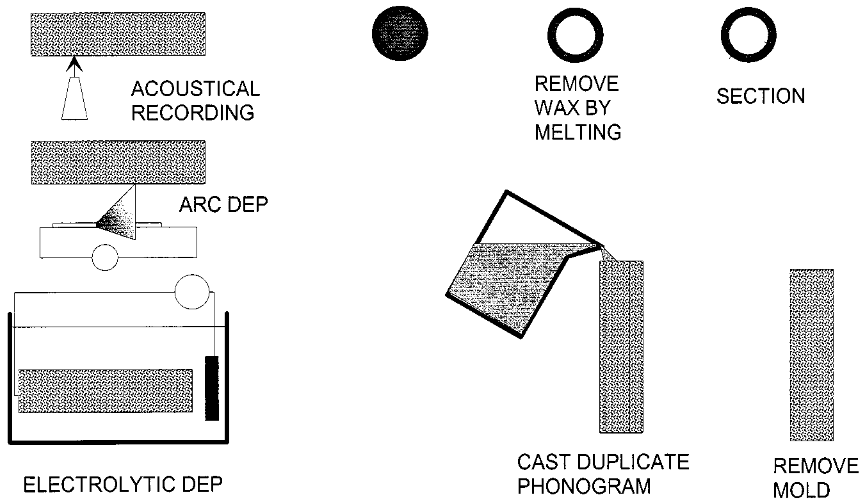

Fig. 2. Edison's method for duplicating phonograms. Sound track is recorded onto wax master cylinder. A conductive seed layer is deposited from a vacuum arc and used as a base for a thick electrolytic deposition. The wax is removed by melting, leaving a free-standing thick metal coating containing the sound track on its inner surface. The coating is sectioned and used as a mold for casting wax duplicate phonograms.

because of the attractive gold color of the TiN coatings which were produced by it. Since then, worldwide interest in VAD has gown exponentially, with several commercial companies selling equipment and/or providing coating services, many factories employing VAD in their production lines and research laboratories developing new VAD coatings, techniques, and apparatus.

While the early work of Wright and Edison had negligible influence on modern VAD development, nonetheless the early pioneers' achievements anticipated later work. Wright used magnetic energy storage to power his pulsed arcs, used substrate motion to obtain uniform coatings, and deposited multilayer coatings. Edison used a hybrid PVD/electrochemical deposition process. Furthermore, Edison initiated the debate about continuous versus pulsed VAD, which has reappeared currently and vigorously defended his patents by litigation [5], as has reoccurred in modern times in this industrial sector.

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Raymond L. Boxman (M'75–SM'77–F'89) received the B.S. and M.S. degrees in electrical engineering from the Massachusetts Institute of Technology (M.I.T.), Cambridge, in 1969, and the Ph.D. degree from M.I.T. in 1973. He was a cooperative student at the General Electric Company (GE) in Philadelphia, and the subject of triggered vacuum gaps became the topic of his M.S. thesis, while laser interferometic measurement of electron and vapor densities in a vacuum arc became the topic of his Ph.D. dissertation.

He was a Senior Research Engineer at GE, where he investigated the behavior of vacuum arcs in high current switches from 1973 to 1975. In 1975, he joined the Faculty of Engineering at Tel Aviv University (TAU), Israel. He is the co-founder of the Electrical Discharge and Plasma Laboratory at TAU. During the last decade, he has focused his research work on the application of the vacuum arc to the production of thin films, and he founded the Israel Plasma Science and Technology Association. He also serves as Associate Editor of the IEEE TRANSACTIONS ON PLASMA SCIENCE, and has been a guest editor for special issues on vacuum discharge plasmas and plasma deposition, and is a member of the Editorial Board for Plasma Chemistry and Plasma Processing. He organized and edited the "Handbook of Vacuum Arc Science and Technology," which involved the coordinated efforts of 24 authors in seven countries. In addition, he has presented over 200 scientific papers at conferences or in technical journals, as well as seven patents.

In 1984, Dr. Boxman and his colleagues were awarded the Joffee Foundation Award by the International Union of Surface Finishing for their work on pulsed vacuum arc deposition. In 2000, he received the Walter Dyke Award from the International Symposia on Discharges and Electrical Insulation in Vacuum. He served as Secretary of the Permanent International Scientific Committee of the International Symposia on Discharges and Electrical Insulation in Vacuum, and as a member of the Program Committee and Session Chairman for the Hard Coatings and PVD Symposium of the International Conference on Metallurgical Coatings and Thin Films.