Donald M. Mattox, Technical Director • Society of Vacuum Coaters
71 Pinon Hill Place N.E. • Albuquerque, NM 87122
505/856-7188 • FAX: 505/856-6716 • www.svc.org

History of Vacuum Coating— Sputter Deposition: Early Efforts

Dr. Arthur W. Wright, professor of molecular physics and chemistry, Yale College, should be recognized as the founding father of vacuum coating technology with his pioneering work.* Several investigators before Wright had recognized and reported the sputtering ("cathodic disintegration," "electrical evaporation") phenomena, but none seems to have pursued the observation with respect to film formation. Wright appears to be the first investigator who built special equipment for depositing films, and then systematically studied a number of vacuum deposited metal films for their optical properties. He reported his finding in two papers published in the *Journal of Science and Art* in 1877 and 1878.[1]

From the late 1850s, gas discharge ("silent discharge") tubes were widely produced, and optical spectroscopy was an emerging scientific study. Before the advent of cold traps in the 1890s, the plasma in the gas discharge tube was always contaminated with mercury from the mercury piston pumps being used to evacuate the gas discharge tube. Wright was interested in using gold to amalgamate ("getter") with the mercury in the gas discharge tube to eliminate the mercury contamination. He noticed that gold placed on the cathode of the gas discharge tube was vaporized and deposited on the walls of the tube, giving a very reflecting surface as seen through the glass. The "cathodic disintegration" phenomena in gas discharge tubes had been reported previously by a number of investigators, including W.R. Grove (England 1852), M. Faraday (England 1854), and J. Plücker (Germany 1858). Vacuum gas discharge studies began shortly after the development of the Ruhmkorff induction coil (iron core transformer with a periodic interrupter in the primary circuit, H.D. Rhumkoff 1851), which generated pulses of very high voltages. These studies increased in number after the development of Pt-glass seals (Geissler 1857) that allowed better vacuum sealing.

** Note: To be a "pioneering" work as far as application is concerned, I mean that the work was pursued with "vigor" by the initial investigator or other contemporaries, and that the initial work was recognized by future investigators.*

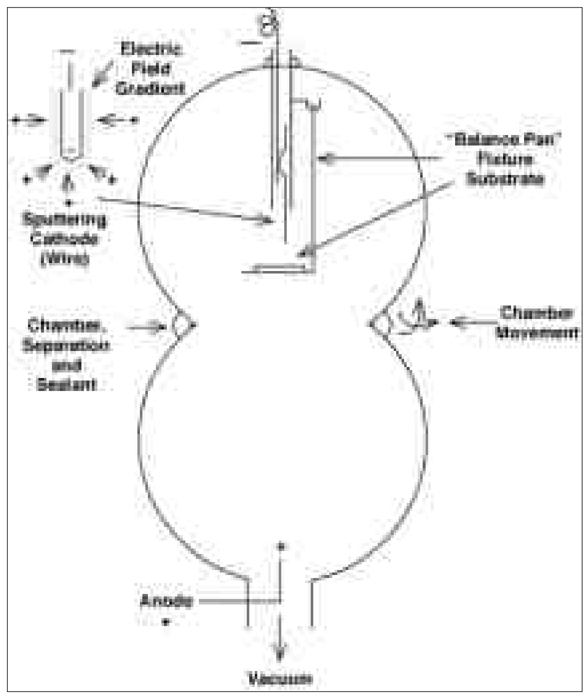

Fig. 1—Interpretation of A.W. Wright's second "electrical deposition" apparatus, 1878 (by Don Mattox).

In Wright's first paper, he referred to work that Faraday had done previously using a spark discharge in a hydrogen atmosphere to deposit metal (particle) films on glass and then study their optical properties.[2] Wright did not mention any previous work on the deposition of films by "cathodic disintegration" or "electrical evaporation" (sputtering), though he must have been aware of the various studies using gas discharge tubes.

In his first paper, Wright studied a number of metal films deposited on the glass tube near the cathode in a standard gas discharge tube configuration, and noted their optical properties through the glass (*i.e.*, as second surface mirrors). In his second paper, he describes a unique deposition system that allowed the deposition of films on glass surfaces that could then be removed from the deposition chamber and analyzed. Figure 1 shows an interpretation of the second system that he described.

The sputtering target was the tip of a wire that could be changed without having to redo the glasswork. Because of the focussing effect of the field curvature around the wire tip on ion bombardment, the tip provided the highest sputtering rate region. The high bombardment rate allowed materials, such as aluminum and magnesium, to be sputtered with difficulty. Actually, mercury contamination in the discharge tube may have aided the sputtering process, since mercury has a vapor pressure of about 1.2 mTorr at room temperature.

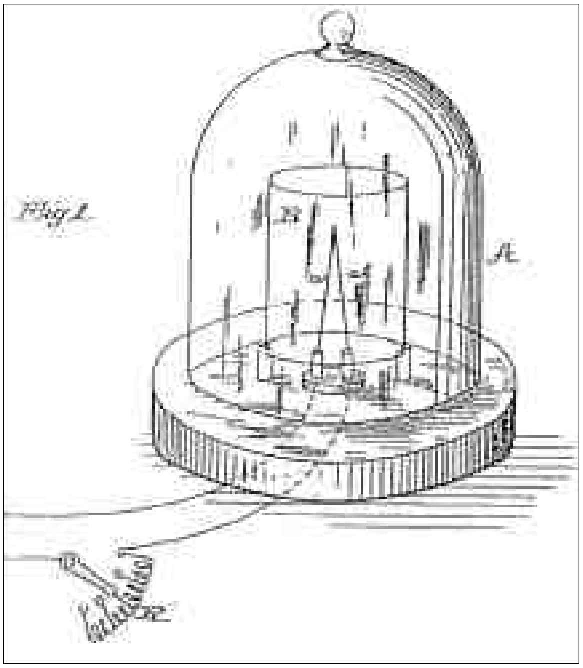

Fig. 2—Fig. 1 of Edison's patent #526,147. "Referring first to Fig. 1, A is the exhausted bell-jar of an air pump and B is a hollow glass placed therein. Electrodes a, a, of the desired metal are placed in the cylinder with their leads a little apart or very slightly in contact so that an arc is formed between the electrodes. An adjustable resistance R may be placed in the circuit to regulate the current."

The substrate fixturing that Wright used was rather unique. The substrate holder is like the pan and pan holder of a beam balance, as shown in Fig. 1. By slightly tilting the vacuum chamber, the sputtering tip could be positioned over various parts of the substrate. This allowed a more-or-less uniform film to be deposited on the glass surface.

Wright's observations on the optical properties of the thin films and their deposition difficulty are summarized in the accompanying table.[3]

Wright's work was used by the U.S. Patent Office to challenge Thomas Edison's patent, "Art of Plating One Material on Another (#526,147)," which was filed in 1884 and finally granted in 1894. The challenge was to Edison's claims for arc vaporization. The 10-year discussion with the U.S. Patent Office was quite extensive.[4] Edison, who really did describe arcing in his patent (low-voltage supply and the wire electrodes starting out in physical contact), finally was granted his patent after terming Wright's process a "periodic arc"—whereas, his was a "continuous arc." Figure 2 shows Fig. 1 of Edison's patent. Edison also called Wright's work a "laboratory experiment not suitable for commercial use." With Wright using a high-voltage low-current Rhumkoff-type coil (as used for gas discharges), and Edison probably using a low-voltage high-current battery, Wright's deposition rate would be slow with a long duration, while Edison's deposition would be fast and short.

Some authors maintain that Edison used the arc vaporization technique to coat his wax phonograph masters with a "seed layer" of gold. The seed layer

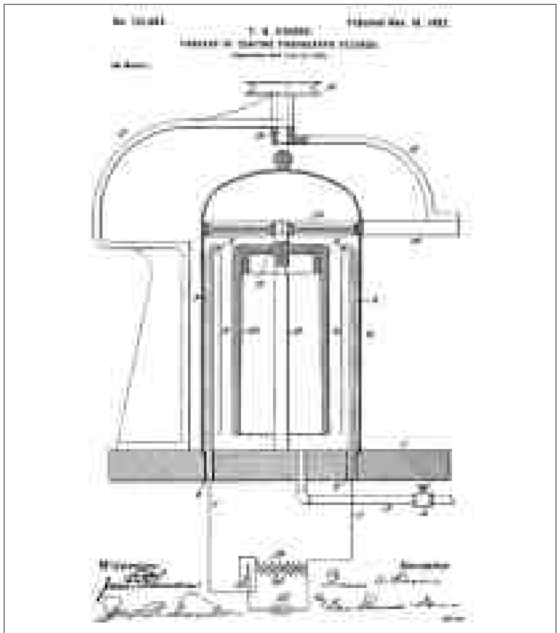

Fig. 3—Fig. 1 from Edison's patent #713,863 (Nov. 18, 1902) "Process for Coating Phonograph Records."

Optical Properties of Thin Metal Films Deposited by Wright, Grouped by Ease of Deposition (from Ref. 3).

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-smokey brown		Feeble
Sn	Brown-gray, sepia		Poor
Zn	Deep grayish blue	Wt-silver	Brilliant
Cd	Deep grayish blue	Wt-silver	Brilliant
Cu	Dull green		Fine
Fe	Neutral (brown tinge)		Brilliant
Ni			
Co			
Al	Brownish		
Mg	Grayish-blue		

Reproduced with permission from the Society of Vacuum Coaters.

was then built up in thickness by electroplating to form the master for production of celluloid phonograph cylinders (1892 patent #484,582 that referred to "vaporizing metal in a vacuum"). However, in his 1902 patent ("Process of Coating Phonograph Records" #713,863), Edison said: "I find in practice that the employment of an electric arc for vaporizing the metal, as suggested in my patent, is open to the objection of being slow, and unless the process is carried out with great care the deposit is not entirely uniform, while there is danger of injuring the very delicate phonograph record surface, particularly from the heat of the arc. I

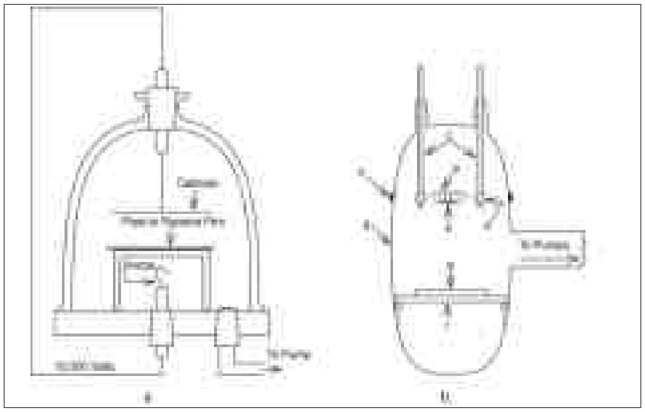

Fig. 4—1(a) Apparatus for the production of mirrors by cathode sputtering; "This method for the preparation of reflecting surfaces is particularly useful as a process for half-silvering and for depositing metals other than silver." "For joint grease a special solution of crude rubber and lard was made." "A 10,000-volt transformer furnishes the current; and it is advisable, although not absolutely necessary, to rectify the current…." 1(b) Apparatus for the production of mirrors by evaporation of metal. "This method of deposition has not been widely tested, and its possibilities are, therefore, little known, but it would seem to be especially valuable for small work where films of any volatile substance are required." "The glass tube may be made entire, then cracked off at (h) and subsequent sealings be accomplished with sealing wax."

find that the rapidity of the process is increased and the character of the deposit improved if the vaporization of the metal is effected by maintaining between two electrodes of the metal a silent discharge of electricity of high tension, such as may be produced from an induction-coil of large capacity or from any induction-machine of approved type, such as the Helmholtz induction-machine."

Figure 3 shows Fig. 1 in the patent and shows what is obviously a sputtering electrode (9 in the patent, wire or foil). Edison may very well have gotten the idea from Wright's work. The figure also shows a rotating substrate fixture driven by an external, rotating magnet. Edison also used sputtering for making free-standing foils (1915 patent).

Wright's work seems to be well known after 1877, and Crookes refers to his work in his paper, "On Electrical Evaporation," in the 1891 *Scientific American Supplement*. Sputtering was in common use in the early 1900s to make mirrors with metals other than silver, which was deposited by chemical means (U.S. Bureau of Standards Circular #389, How to Make Mirrors 1931). In the mid 1930s, thermal evaporation became the common way to make mirrors. Figure 4 shows sputtering and thermal evaporation configurations as taken from the U.S. Bureau of Standards Circular #389.

Sputter deposition on webs began in about 1930[5] with sputter deposition of silver on silk (unknown maker, Leipzig, Germany), followed by the preparation of gold stamping foils by deposition on glassine (semi-transparent waxed paper) in 1934 (Whiley [England]; Kurtz [Germany]). Also in 1934, the Hy-Sil Company of Boston, MA, bought a web coater from a Belgium company to coat silver on cellophane for decorative purposes, and the Bosch Company (Germany) began metal-coating paper to make paper capacitors. By the late 1930s, thermal evaporation had replaced sputtering as a vapor source for most vacuum coating applications, until the advent of magnetron sputtering in the early 1970s.

There seems to be some confusion as to whether Wright, who called his process "electrical vaporization," was using sputtering or (gaseous) arcing.[3] Part of the problem was that Wright was not very specific in his description of the electrical parameters of the deposition process he used, although he did say that he used an induction coil and that the discharge power must not be so high as to have a "disruptive character, since this deposits some of the material in the form of a powder." At that time, vacuums were not good enough to have true vacuum arcs, but arcs could form by first having a gas discharge that then broke down into an arc, though the power conditions for the two situations are quite different. Professor Wright seems to be the first to study vacuum coating seriously. Evidence indicates that he used sputtering to vaporize the material that he deposited, and that subsequently this method of deposition was used to form mirrors for various applications.

The Wright-Edison patent situation is a prime example of the difficulty of having two very different sources of information. The publicity over Edison's patent was probably one reason some authors have considered Wright's work to be arc vaporization. ***P&SF***

References

1. A.W. Wright, "On the Production of Transparent Metallic Films by the Electrical Discharge in Exhausted Tubes," *American Journal of Science and Arts*, Vol. 13, pp. 49-55, 1877; & A.W. Wright, "On a New Process for the Electrical Deposition of Metals and for Constructing Metal-covered Glass Specula," *American Journal Science and Arts*, Vol. 14, pp. 169-178, 1878.
2. Michael Faraday, *Experimental Researches in Chemistry and Physics*, 1859.
3. Raymond L. Boxman, "Vacuum Arc Deposition: Early History and Recent Developments," Invited Dyke Award and Lecture, *Proceedings of XIXth Symposium on Discharges & Electrical Insulation in Vacuum (IEEE)*, pp. 1-8, Xi'an, China, Sept. 18-20, 2000; also *Handbook of Vacuum Arc Science and Technology: Fundamentals and Applications*, edited by Raymond L. Boxman, Philip J. Martin & David M. Sanders, p. xii, William Andrew/Noyes, 1995.
4. Thomas A. Edison Papers Project, Rutgers Univ. (www.edison.rutgers.edu).
5. E.O. Dietrich & R. Ludwig "Vacuum Web Coating—An Old Technology With a High Potential for the Future" *Society of Vacuum Coaters, 40th Annual Technical Conference Proceedings*, pp. 354-364, 1997.