Vacuum Coating—An Enabling Technology

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ABSTRACT

Vacuum (sub-atmospheric) coating processes have been the enabling technology in several fields for a number of reasons. The vacuum coating process has allowed a functional coating to be deposited when no other technique can do so and sometimes has allowed the production of a more functional coating than is available by other means. The use of a vacuum coating can provide a more marketable product that is produced at a low cost. In some cases the reproducibility of the process allows the production of very complex and demanding products such as multilayer diffraction gratings and bandpass filters. New markets have been generated due to the availability of vacuum coating processes. In many, if not most cases, a vacuum coating is a value-added process whose price and contributions to the economy and the environment is difficult to quantify. This presentation will address many of these subjects and compare some vacuum coated products to non-vacuum-coated products and processes. In the past few years, plasma-based vacuum processes have become important production techniques and their use is expanding rapidly. Vacuum coating technologies will continue to develop and be an enabling technology for the foreseeable future.

INTRODUCTION

An "enabling technology" is one that allows something to be done on an industrial scale that could not be done otherwise. The first use of vacuum coating (sputter deposition) on an industrial scale was by T. Edison for making the sub-masters of his "Gold Moulded" cylinder records. However, the process was not an enabling technology because others were doing much the same thing by making their wax masters electrically conductive using carbon powder.

The second early process that might be considered enabling was the zinc coating of paper for paper capacitor by R. Bosch (Bosch Company) in 1935. The use of metallized paper (roll coating) instead of metal foil allowed the size of a capacitor to be reduced by about 50%. In 1940 Whiley (England) patented the use of aluminum for web coating. Lead foil was used for early packaging to some extent but tin foil was the first widely used flexible packaging foil. It was replaced by aluminum foil after 1910 when repeated rolling of aluminum was shown to provide a cheaper foil product. Aluminum foil was used to preserve "freshness" until well after WWII when it was replaced by metallized polymer film prepared by vacuum coating.

Web coating went on to be an enabling technology for such processes as coating polymer with vapor barriers for flexible packaging. Multilayer coatings on webs began in the IC industry to metallize flexible substrates. A major advance in web coating was the use of sputter deposition for depositing compounds and multilayers. For packaging this is leading to "see-through" freshness packaging. Magnetron sputter deposition on flexible webs was first used by D. Charoudi in 1977.

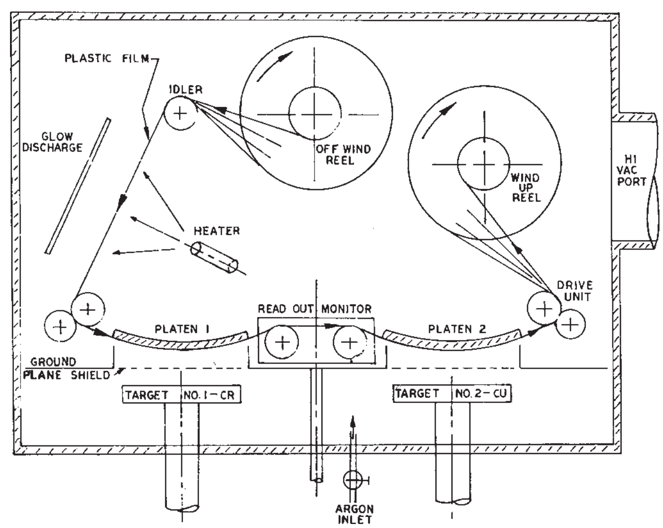

Figure 1: RF sputter deposition of Cr and Cu on a Kapton® web, (Morrill, Egan, Paszek, and Aronson) JVST 9(1)350 (1972)

The antireflection (AR) layer on old glass was recognized in the early 1800s. In the latter part of the 1800s all professional photographer knew that old lenses were better than new lenses because of the coating that formed on them with age. There were numerous attempts (and patents) on the chemical treatment of lenses to form an AR coating on the surface.

In 1935 A. Smakula (Zeiss Company) discovered the use of vacuum coating to form single-layer AR coatings on lenses but the patent was considered to be a Military Secret until 1940 [1]. In 1936 John Strong discovered the use of vacuum coating for forming an AR coating on lenses and published it in the open literature. Again this might be considered an enabling technology even though chemical treatments can be used to formed AR coatings on surfaces. It is interesting to note that the Germans did not use AR coatings on camera lenses until after WWII. Single-layer AR coatings continued in use well after WWII [2].

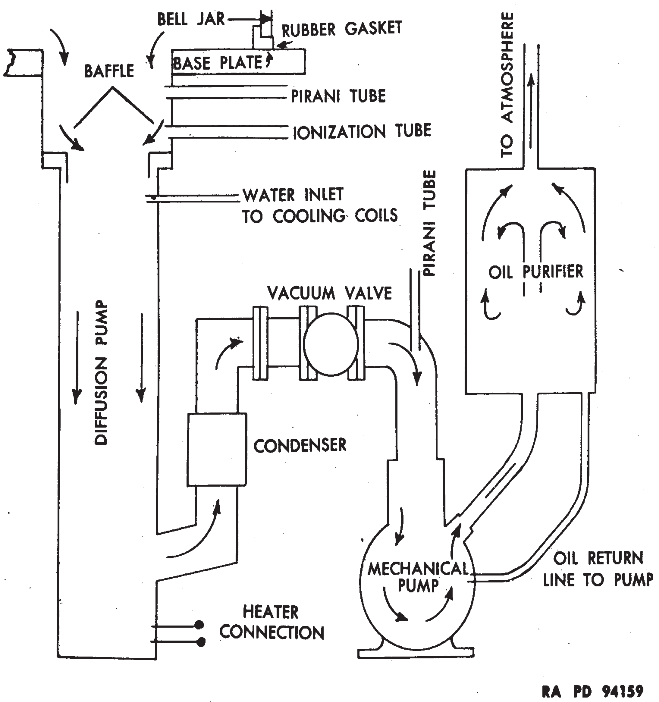

Figure 2: American vacuum system for coating optics during WWII. Note the lack of a high vacuum valve.

The first explanation of the effect of a single-layer coating on antireflection was by Airy in 1832 [3]. He used classical ray and wave techniques to show the effect. In 1939 using chemical techniques (Langmuir- Blodgett films) to form layers of very precise thickness and varying indices of refraction Blodgett showed the AR effect and equations for the relationship between thickness and index of refraction in AR coatings [4].

Multilayer AR coatings are another matter. Cartwright and Turner deposited 2-layer coatings in 1939. There is one report that the Schott Co. (Germany) formed multiplayer AR coatings (3-layer) on lenses during WWII by spray pyrolysis. Otherwise mutilayer AR and filter coatings were not used until the late 1940s.

It has been asserted that Monarch Cutler, an undergraduate student at MIT, was the first to calculate the effect of multicoatings on the AR properties of a surface [5]. Mr. Cutler's senior thesis at MIT was entitled "*Reflection of Light From Multilayer Films* (May 1939). It is interesting to note that in the acknowledgment of his thesis Mr. Cutler acknowledged Dr. Cartwright and Dr. Turner "for information concerning their work in the production of color films." He also acknowledged Richard P. Feynman, also an undergraduate student at MIT, for his help in deriving the equations for the reflection and transmission of multilayer films. Dr. Feynman later received a Nobel Prize in Physics (1965) for his work in quantum electrodynamics (QED) and was considered one of the finest physics lecturers of all time [6]. Feynman's senior thesis at MIT was "*Forces and Stresses in Molecules*." In my research I have not found any other reference to a relationship between Dr. Feynman and Mr. Cutler's 1939 work. By 1946 several authors were involved in calculating the optical properties of multi-layer films [7].

The vacuum deposition of aluminum reflecting coatings on glass by vacuum deposition can certainly be considered an enabling technology for the subject of astronomy. John Strong published the first work on aluminizing large mirrors in 1936 [8]. For about 100 years before that time chemical deposition was used. The "modern" techniques of deposition by chemical reduction began with Liebig in 1835 [9]. There are two widely used methods of chemical silvering. The "Brasher method" was used to deposit thick coatings on front-surface mirrors that could be subsequently polished for telescope mirrors and the "Rochelle Salts method", that has a slower deposition rate, and was used to deposit thin silver films such as were used in partially silvered mirrors.

In 1920 at a discussion on "The Making of Reflecting Surfaces" R. Kanthack, in his Introduction, stated "Six weeks of bibliography hunting have given me the impression that at the present time –85 years after Liebig's classical discovery! – we have not evolved any method of chemical deposition on glass so scientific and practically perfect that it could be adopted officially" [10].

Polishing, which leaves minute scratches, reduces the resolution of the reflected light as was shown in tests by Strong on the Hooker 100 inch telescope on Mount Wilson in the mid-1930s. The Hooker telescope had used polished chemical-silver coatings and had barely been able to see the companion star (magnitude of 8) of the extremely bright star Sirius (magnitude of minus 1.5). Strong's vacuum evaporated aluminum coating enabled the "Companion of Sirius" to be resolved easily by the Hooker telescope. During WW II Heraeus (Germany) used the sublimation of a protective layer of SiO on the surface of aluminized mirrors. In 1946 Turner addressed the effect of a single layer dielectric on mirror surfaces ("protected" surfaces). Today multilayer reflecting coatings are used in all kinds of reflecting applications. These include heat mirrors, cold mirrors, low-E window coatings, silver coatings on astronomical telescopes and many others.

Corrosion protection is one of the most demanding applications for coatings of any type. Electroplating on electrically conducting substrates was developed soon after the development of the Volta Cell in 1800 and has been used to deposit corrosion protective coatings for many years. A problem with the electrodeposition of many materials from aqueous solutions is the co-deposition of hydrogen. This hydrogen can cause embrittlement of high strength steels (>200,000 psi), particularly when they are under stress. The electroplating industry uses heating to try to outgas the incorporated hydrogen but this can be difficult to quantify. Vacuum deposited cadmium (VacCad) was formally accepted as a replacement for electrodeposited cadmium by the military in 1958 (Mil Spec. 8837) as a sacrificial corrosion protective coating.

A major advance in corrosion resistant coatings was the development of the "Ivadizing" process at McDonnell-Douglas in the late 1960s. The ivadizing process allowed adherent evaporated aluminum to be coated on steel and titanium fasteners in a "barrel coater." These coated fasteners prevent galvanic corrosion when they are used in contact with aluminum such as on airplane "skin." The process was later just called "ion vapor deposition" and is now known in the aerospace and military related industries as IVD coating. The aluminum deposited by IVD is often shot peened or burnished in order to seal pinholes that are a problem with using vacuum coatings for corrosion protection.

Vacuum coating for tribology, using low-shear-strength metals, was studied and developed by NASA for use in vacuum in the late 1960s. Their advantage is that they do not "creep" as oils and greases do. An example of their current use is in the coating of bearings used on the rotating anode in x-ray tubes,

Vacuum deposition of electrical resistors didn't come into real use until the age of the "integrated circuit" (IC) technology. The IC industry began in the late 1950s. In IC technology tantalum was a material of great interest for making stable thin film conductors with low temperature coefficient of resistivity (after annealing), thin film resistors made of reactively sputter deposited TaN that could easily be "trimmed" to the correct resistance values by anodizing, and thin film capacitors that could be made by anodizing (oxidizing) the film surface to form a dielectric (Ta_2O_3). For the IC industry very high volumes of coated substrates were needed.

The IC industry brought about the introduction of high-volume coating systems such as the air-to-air in-line coater [12], the load-lock in-line coater, and the random-access process chambers with a central vacuum chamber [13] that may be considered the forerunner of the modern cluster tool that is widely used for processing wafers.

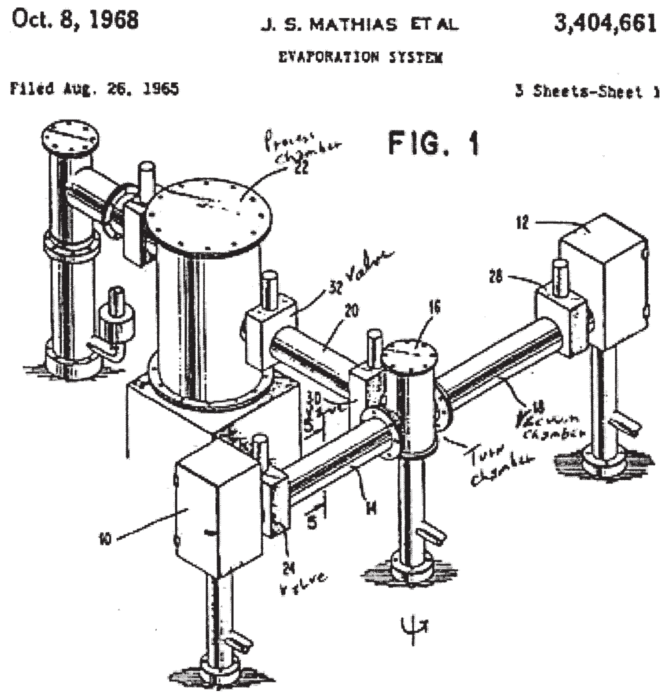

Figure 3: Patent for a vacuum system with a central vacuum chamber and separate processing chamber. This may be considered the forerunner of the cluster tool [13].

Sputter cleaning is an *in situ* cleaning process that is often integral to obtaining good adhesion of the deposited coating. Sputter cleaning was first used in ultrahigh vacuum technology in the field of Surfaces Science to obtain atomically clean surfaces. Sputter cleaning as a separate step in vacuum coating is often not as successful as it could be because of recontamination of the surface between processing steps. An enabling technique was introduced in the early 1960s whereby the sputter cleaning was continued while the first of the coating material was applied by evaporation. As long as the deposition rate exceeded the sputtering rate a film was formed, essentially on an atomically clean surface.

SUMMARY

There are a number of developments in vacuum coating technology that might be cited as "enabling technologies" but the following would certainly be included in any list.

1. Evaporation of aluminum from tungsten filaments.
2. Deposition of single-layer and multiplayer optical coatings.
3. Development of electron beam (e-beam) evaporation techniques.

4. Use of concurrent bombardment during deposition to modify the properties of the deposited material.
5. Integration of the sputter cleaning process with the deposition process to give a "clean" interface.
6. Development of reactive sputter deposition.
7. Development of the in-line deposition system ("tool").
8. Development of magnetron sputter deposition technology.
9. Development of plasma enhanced chemical vapor deposition (PECVD) technology.
10. Development of arc vapor deposition.

ACKNOWLEDGMENTS

Thanks to Ric Shimshock for pointing out the very interesting relationship of Richard P. Feynman to Monarch Cutler and providing the title page of the Cutler thesis. Thanks to George Dobrowolski for calling my attention to the Russian work (ref. 12) that describes 2-layer AR coatings and providing the translations given in ref. 12 and Appendix 1.

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12. S.S. Charsan, R.W. Glenn and H. Westgaard, The Westen Electric Engineer, 7, 9 (1963)

13. Joseph S. Mathias, Alfred A. Adomines, Richard H. Storck, and John McNamara "Evaporation System" U.S. Patent #3,404,661 (Oct. 8, 1968) (filed Aug. 26, 1965)

APPENDIX 1

May 3, 2004
To: Don Mattox
Below is the Russian original and the English translation (in brackets) of the contents of the title page of the book which I am also appending in the form of a file for your interest:

Academician I.V. Grebenshchikob, A.G. Vlasov, B.S. Neporent, N.V.
Suikobskaya

The antireflection coating of Optics/ Reduction of the reflection of light by the surfaces of glass (Prosvetlenie Optiki/ Umienshenie otrazheniya sveta poverchnost'yu stekla), edited by I.V.Grebenshchikov, published by Gocudarstvennoe Izdatelstbo Technicko-Teoreticheskoi Literaturyi (State Publishers of Technical-Theoretical Literature) Moskva 1946 Leningrad

The book consists of 212 pages and is organized in 9 chapters with headings:

1. Physical basis for the antireflection effect
2. Mathematical theory of the antireflection effect of thin films
3. Physical properties of antireflection coatings and their control
4. Antireflection coating of silicate glasses using an etching method
5. Antireflection of glasses by deposition of silicon-organic solutions
6. Deposition of antireflection coatings through the deposition of fluoride vapors in a vacuum
7. Antireflection though the deposition onto the surface of a glass of monomolecular layers of organic materials
8. The manufacture of glasses with an enhanced reflection coefficient through the deposition of titanium dioxide layers
9. Antireflection coating through the deposition of two-layer coatings.

It contains 99 illustrations (some of equipment), tens of tables, and over a hundred references. Very impressive for a book which must have been written during the Second World War, if it was approve for publication in March of 1946 and came out later in the same year.

George Dobrowolski