

Tracing the 5000-year recorded history of inorganic thin films from similar to 3000 BC to the early 1900s AD

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APPLIED PHYSICS REVIEWS

Tracing the 5000-year recorded history of inorganic thin films from ~3000 BC to the early 1900s AD

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Gold is very likely the first metal discovered by man, more than 11 000 years ago. However, unlike copper (~9000 BC), bronze (~3500 BC), and wrought iron (~2500–3000 BC), gold is too soft for fabrication of tools and weapons. Instead, it was used for decoration, religious artifacts, and commerce. The earliest documented inorganic thin films were gold layers, some less than 3000 Å thick, produced chemi-mechanically by Egyptians approximately 5000 years ago. Examples, gilded on statues and artifacts (requiring interfacial adhesion layers), were found in early stone pyramids dating to ~2650 BC in Saqqara, Egypt. Spectacular samples of embossed Au sheets date to at least 2600 BC. The Moche Indians of northern Peru developed electroless gold plating (an auto-catalytic reaction) in ~100 BC and applied it to intricate Cu masks. The earliest published electroplating experiments were ~1800 AD, immediately following the invention of the dc electrochemical battery by Volta. Chemical vapor deposition (CVD) of metal films was reported in 1649, atmospheric arc deposition of oxides (Priestley) in the mid-1760s, and atmospheric plasmas (Siemens) in 1857. Sols were produced in the mid-1850s (Faraday) and sol-gel films synthesized in 1885. Vapor phase film growth including sputter deposition (Grove, 1852), vacuum arc deposition (“deflagration,” Faraday, 1857), plasma-enhanced CVD (Barthelot, 1869) and evaporation (Stefan, Hertz, and Knudsen, 1873–1915) all had to wait for the invention of vacuum pumps whose history ranges from ~1650 for mechanical pumps, through ~1865 for mercury pumps that produce ballistic pressures in small systems. The development of crystallography, beginning with Plato in 360 BC, Kepler in 1611, and leading to Miller indices (1839) for describing orientation and epitaxial relationships in modern thin film technology, was already well advanced by the 1780s (Häuy). The starting point for the development of heterogeneous thin film nucleation theory was provided by Young in 1805. While an historical timeline tracing the progress of thin film technology is interesting of itself, the stories behind these developments are even more fascinating and provide insight into the evolution of scientific reasoning. © 2014 AIP Publishing LLC.

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I. INTRODUCTION: ANCIENT METALLURGY

While there is no definitive archeological proof, it is highly probable that gold was the first metal to be discovered by man since it is readily available in a relatively pure state. No extractive metallurgy is required; gold is easily recoverable from placer deposits. Many rivers worldwide contain gold which can be washed from the bank sands, where it has been concentrated for millennia, by the action of water slowly eroding rock containing primary gold deposits. If this hypothesis is correct, it would place the discovery of gold more than 11 000 years ago, the date now generally accepted for the oldest surviving copper artifacts.¹

The discovery of native copper is estimated to have occurred ~9000 BC in the ancient Near East;¹ a copper pendant (Figure 1) found in northern Iraq dates to 8700 BC.²⁻⁴ Based upon both archeological evidence and metallurgical analyses, copper smelting (extraction from ore), and metal working appear to have originated independently in the Balkans (Serbia and Bulgaria) ~5500 BC and in Anatolia by at least 5000 BC.⁵⁻⁸ Figure 2 is a photograph of copper slag from a Serbian Vinča (a Neolithic culture) archaeological site occupied from ~6000 to 4600 BC.⁷ Slag, typically a mixture of metal oxides and silicon dioxide [SiO₂], is a byproduct of extractive metallurgy. Note the embedded green copper droplets in Figure 2. An idol, discovered at a Vinča site on a plateau in eastern Serbia, is shown in Figure 3. It was produced ~5000 BC from smelted copper by beating. Float copper, found in glacial drift deposits, was utilized by Native Americans for tools, knives, fishhooks, and ornaments in the Great Lakes region of the northern mid-west United States and southern Canada between 6000 and 3000 BC.⁹ However, there is no evidence of smelting.⁹ A site in Keweenaw County, Michigan, contains copper artifacts dating to ~7800 BC.

A spectacular example of excellent metallurgical and artistic craftsmanship is shown in Figure 4, a picture of the famous Copper Bull statue, produced ~2600 BC and found near the Mesopotamian city of Ur (now southern Iraq) and presently in the British Museum, London.¹⁰ Alloying copper

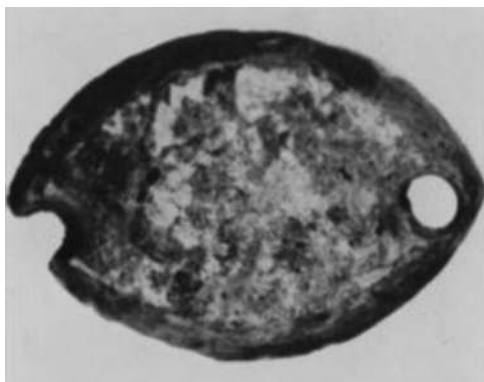


FIG. 1. A copper pendant produced ~9000 BC from adventitious Cu by beating. It is 2.3 cm long \times 0.3 cm thick and was found in Mesopotamia (Shanidar Cave, northeast Iraq). Adapted from Ref. 2.



FIG. 2. Copper slag from Belovode (sample No. 21), on a plateau in Eastern Serbia, with embedded green copper droplets. The slag dates from ~5000 BC. Adapted from Ref. 7.

with tin to produce bronze, a much harder material, was known by at least 3500 BC (copper-arsenic was developed even earlier, between 5000 and 4000 BC, southeast Iran).¹¹ Copper-tin bronze artifacts dating to 3000 BC have been found in Sumeria (Mesopotamia) and Egypt;¹² somewhat later, 2700–2300 BC, in the upper Yellow River area of China.¹³ Iron smelting has been traced to ~3000–2700 BC in Asmar, Mesopotamia,¹⁴ although adventitious iron (alloyed with nickel) from meteorites may have been used even earlier for tools and weapons.¹⁵

Gold has occupied a unique role in man's history. Even though gold was discovered early, it was not until very recently (paradoxically, after the abolition of the gold standard backing monetary currency) that it has been used in technological applications such as microelectronics. Early man did not utilize gold for tools or weapons (it is too soft to replace stone and flint). In fact, gold had only two properties that made it valuable at that time: a bright yellow color which does not corrode or oxidize and extreme malleability



FIG. 3. A Chalcolithic (Copper Age) idol produced from smelted copper ~5000 BC. Photograph courtesy of the Apsara Gallery, *The Earliest Use of Copper* (<http://apsara.transapex.com/>).



FIG. 4. The Copper Bull statue (61 cm long \times 61 cm high) was found at the Temple of Ninhursag, Tell al-'Ubaid, near the Mesopotamian city of Ur (now southern Iraq) \sim 2600 BC. Photograph attributed to BabelStone licensed under Creative Commons CC0 1.0 Universal Public Domain Dedication. The statue is on display at the British Museum, London, number ME 116740, registration 1924,0920.1.

(when pure), allowing it to be shaped and beaten to thin foils by skilled craftsman. Thus, its primary uses were for decoration, religious artifacts, and commerce (coinage and a show of wealth). The presence and complexity of gold artifacts in ancient burial sites serve as a measure of the technological sophistication of the society.

Archeologists have long known of the rich gold mines, dating to at least 3500 BC,¹⁶ in the Eastern Desert of Egypt and the large number of gold artifacts in tombs at Saqqara and Thebes.¹⁷ In fact, there is a clear correlation between the number of mines being worked in a given period of Egyptian Pharaonic history and the number of gold artifacts discovered. Figure 5 is a map of the Egyptian Eastern Desert showing some of the ancient gold mining sites identified by geologists and archeologists.¹⁶ There are many additional sites south of this area in the Nubian Desert, northeast Sudan. The two areas together are estimated to contain \sim 250 ancient gold production sites; the earliest being open pit mines in which gold in quartz veins was crushed *in-situ* by heavy (6–10 kg) two-handed stone hammers. With time, more sophisticated mining techniques including smaller (2–5 kg) one-handed hammers with stone mortars and

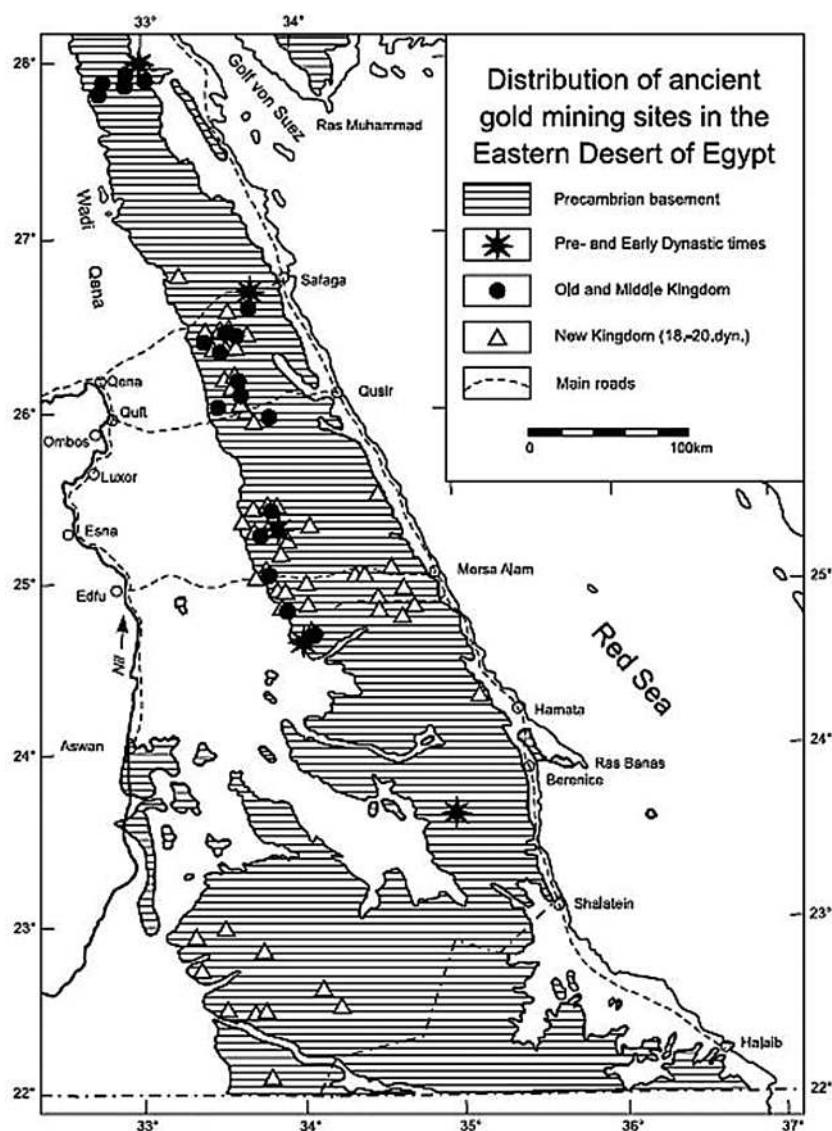


FIG. 5. Map of the Egyptian Eastern Desert showing ancient gold mines identified during a geological/archeological expedition from 1989 to 1993. The symbols represent sites from * Pre- and Early Dynastic times (\sim 3500–3000 BC), ● the Old (2700–2160 BC) and Middle Kingdom (2119–1794 BC), and Δ the New Kingdom (1550–1070 BC). Adapted from Ref. 16.

grinding stones (Figure 6), hydro-metallurgical processes, and milling techniques were introduced.¹⁶

The largest and oldest collection of high-purity gold artifacts was discovered accidentally in 1972; not in Egypt, but at a construction site in Varna, Bulgaria, near the Black Sea, at what is now called the Varna Necropolis, an ancient burial site.^{18,19} The graves have been dated to 4700–4200 BC, consistent with gold working finds in nearby parts of southeast Europe,²⁰ by ¹⁴C isotopic decay measurements. Three thousand gold artifacts were found, with a total weight of ~6 kg and comprising more than 38 different types of objects unique to Varna. The remains of thirteen settlements were found in the local area; the cemetery, the largest in Eastern Europe, is approximately 10 000 m². Figure 7 shows a few of the outstanding ancient gold artifacts,²¹ many of which are on display at the Varna Archaeological Museum.

II. THE FIRST GOLDEN AGE OF THIN FILM TECHNOLOGY, FROM THE ANCIENT EGYPTIANS TO THE ROMANS

The earliest documented inorganic thin films were gold layers produced chemi-mechanically, for decorative (and later, optical) applications, by the Egyptians during the middle bronze age, more than 5000 years ago. Gold films (Au “leaf”), <3000 Å thick, gilded on base-metal statues and artifacts have been found in ancient tombs, including the Pyramid of Djoser (see Figure 8) in Saqqara, southwest of Cairo, Egypt.^{22–24} Today, Au leaf can be beaten to ~500 Å thick (partially transparent to visible light) by highly skilled craftsmen.²⁵ In fact, the production of gold leaf, primarily for decorative purposes, remained a viable industry for craftsmen until the development, in the mid-1930s, of roll-to-roll web coating by sputter deposition and evaporation as described in Secs. IV B 1 b and IV B 4 b.

The Egyptians mined Au ore in the Eastern Desert, between the Nile River and the Red Sea. Ancient mining sites in Wadi Hammamat (along the trade route from Thebes, modern day Luxor, to the Red Sea port of Elim) are accurately located on a papyrus map (Figure 9), drawn in approximately 1160 BC (Refs. 27 and 28) and now on display in the Museo Egizio, Turin, Italy.

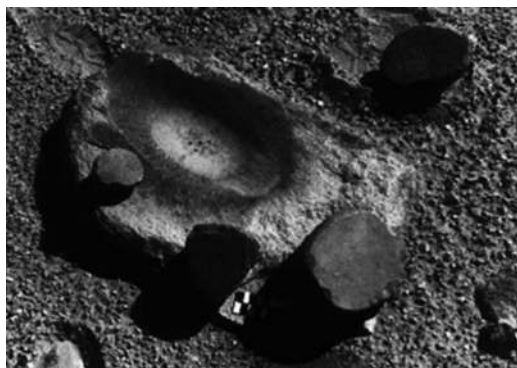


FIG. 6. New Kingdom (1550–1070 BC) oval-shaped andesitic (igneous, volcanic rock) stone mill with several grinding stones; from the Hairiri gold mining site, Wadi Allaqi, southern Eastern Desert, Egypt (the scale, lower middle of the figure, is 10 cm). Adapted from Ref. 16.



FIG. 7. Ancient gold artifacts dating to ~4500 BC from the Varna (Bulgaria) Necropolis. Adapted from Ref. 21.

Ore was purified by melting it in a mixture of “alum” [the mineral alunite, $KAl_3(SO_4)(OH)_6$], salt [NaCl], and chalcopyrite [e.g., $CuFeS_2$] minerals. The process evolves H_2SO_4 and HCl which dissolve the base metals.^{29,30} The purified gold still had several to a few tens of atomic percent of silver, copper, or both, depending upon where it was



FIG. 8. The tomb of Pharaoh Djoser (actual name, Netjerykhet, second King of the Third Dynasty, Old Kingdom; ruled from ~2667 to 2648 BC).²² This is the first pyramid constructed of cut stone (uncut-stone pyramids in Caral, Peru, are of a similar age).²⁶ The Djoser Pyramid was initially 62 m tall, with a base of 109×125 m², and clad in smoothed white limestone.²⁴ Sometimes called the Step Pyramid, it consists of six mastabas (rectangular structures with sloping sides), the first of which is square. Photograph attributed to Roweromaniak, Poland, licensed under Creative Commons Attribution-Share Alike 2.5.

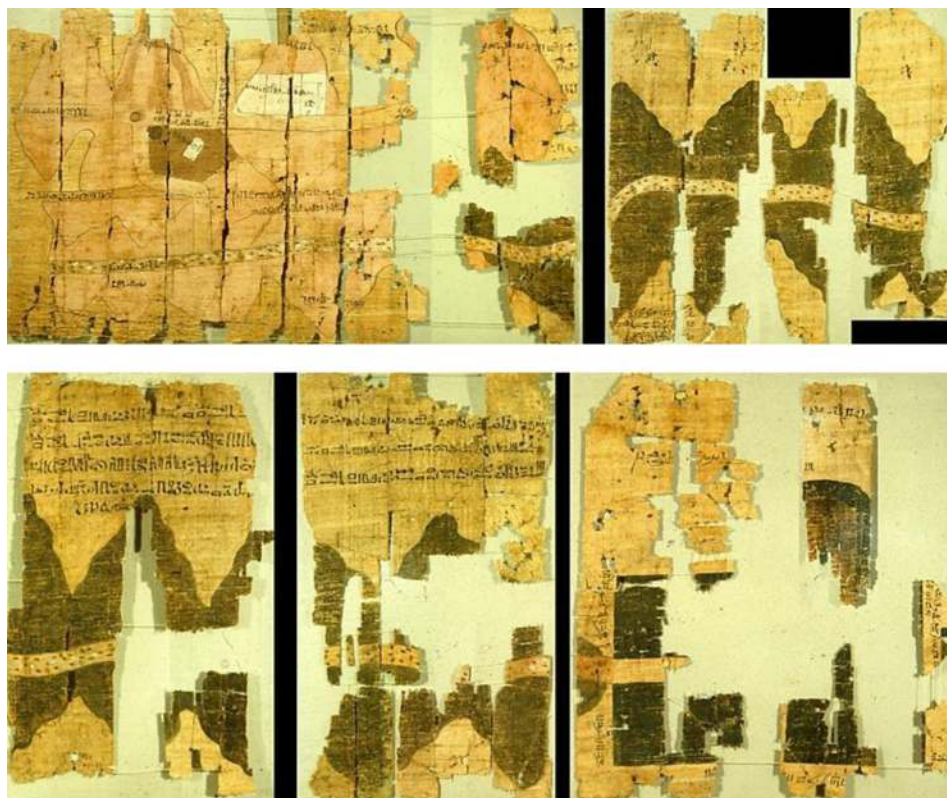


FIG. 9. Pieces of a map of ancient mining sites near Wadi Hammamat (Valley of Many Baths) in the Eastern Desert of Egypt, approximately 70 km from Thebes (modern Luxor). It was drawn by a scribe of Ramses IV during a quarrying expedition, ~1160 BC, which included 8362 men. The top is oriented toward the south, the source of the Nile River. The colors correspond to the actual appearance of the rocks in the mountains.²⁸ Photographs courtesy of Professor James A. Harrell, Department of Environmental Sciences, University of Toledo.

mined, thus giving rise to variations in color. Thinning was initiated by beating with a rounded stone and mechanical rolling, followed by many stages of thinning and sectioning composite structures consisting of Au leaf sandwiched between layers of animal skins, parchment, and vellum.²⁵ Figure 10 is an image from a tomb (~2500 BC) in Saqqara illustrating melting and purification of Au in which the temperature is adjusted using blow pipes. The frieze also shows an initial step in the gold thinning process.

Highly skilled ancient Egyptian artisans mastered the art of gold sheathing at least as early as 2600 BC.^{17,31} Sheathing is the direct application of thin gold layers onto wooden and plaster objects (mostly for noble families) to give the impression that the object is solid gold. Striking examples were found in the tomb of Queen Hetepheres (wife, and



FIG. 10. A fresco from a tomb (~2500 BC) in Saqqara, Egypt, depicting the gold melting and purification process as well as the initial thinning of gold sheets with a rounded stone. The reed blow pipes, tipped with baked clay, were used to both increase and control the temperature of the charcoal fire in the ceramic pot. Adapted from Ref. 31.

half-sister, of Pharaoh Sneferu, Fourth Dynasty, Old Kingdom, ~2613–2589 BC). Other spectacular examples of early thin film technology were found in the tomb of Pharaoh Tutankhamun (“King Tut,” Eighteenth Dynasty, ruled ~1332–1323 BC). Gold sheets were beaten into position over carved wooden structures to provide embossed hieroglyphic text and decorations. An example is shown in Figure 11.

The Egyptians also developed a “cold mercury” gilding process for copper and, later, bronze (copper/tin alloy) statues, jewelry, and religious articles.³³ The basic procedure consists of hand polishing the metal surface, then rubbing liquid mercury into it. Some mercury dissolves into the copper forming a very thin copper/mercury amalgam. The excess mercury is mechanically removed leaving a mirror-like surface. Gold leaf is then press-bonded to the surface, absorbing a small amount of mercury from the copper. The interfacial layer is a very early example of what is today referred to as a film/substrate adhesion layer. The importance of mercury is further highlighted by the finding of a vial of the liquid metal in an Egyptian tomb, dating to the fifteenth or sixteenth century BC, near Kurna on the west bank of the Nile, across from Luxor.^{34,35}

Gaius Plinius Secundus Maior (“Pliny the Elder,” 23–79 AD, a Roman natural philosopher and military commander born near the modern town of Cuomo, Italy), described the cold mercury process in his *Naturalis Historia*, an encyclopedia consisting of 37 books in which he collected much of the knowledge of his time.³⁶ The symbol Hg derives from the Latin word “hydrargyrum” meaning “liquid silver.” The cold mercury process was supplanted by the hot, or fire, mercury process in which heat is used to diffuse mercury into the substrate as well as to vaporize the excess mercury.^{33,37}



FIG. 11. A photograph of Egyptian gold embossing, thin layers of gold covering a wooden structure with raised carved text and decorations, found in the tomb of Pharaoh Tutankhamun (ruled ~1332–1323 BC). Adapted from Ref. 17. A dagger made from adventitious meteoric iron (iron/nickel alloy) was also found in Tutankhamun's tomb, well before the start of the Iron Age in Egypt, characterized by the introduction of iron smelting and the production of iron/carbon steel.³²

The mental and physical toxicity effects of mercury on artisans were known by the ancients. Pliny the Elder³⁶ reported, for example, that slaves who worked in mercury mines often died of mercury exposure. However, the demand for gold gilding was sufficiently high that the practice continued for many centuries. The phrase “mad as a hatter,” coined in 18th century England, describes “mad” workers using mercury to cure felt for making hats.

There is some archaeological evidence that thin-film deposition by electroplating was used in place of metal gilding in Mesopotamia between the last few centuries BC and the first few AD.³⁸ In 1936, archaeologists uncovered, in a village near Baghdad, Iraq, a set of terracotta jars which contained cylinders of copper sheet and iron rods. Copper and iron form an electrochemical couple which, in the presence of an electrolyte, produces a voltage. It is conjectured that a common food acid, such as lemon juice or vinegar, served as an electrolyte. Modern replicas have produced working batteries with voltages of ~0.5–0.9 V. However, there is no definitive proof of the Baghdad battery theory; documented electroplating dates back only a little more than 200 years as discussed in Sec. IV A 1.

The art of joining two metal parts together, with a thin film interfacial layer, by both gold and silver brazing is believed to have been developed around 3400 BC by the Sumerians in the region that later became known as Mesopotamia.³⁹ Brazing (sometimes termed “hard soldering”) is a process for producing a solid joint by means of a filler material with a melting point just lower than that of the

metals to be joined, as opposed to soldering which incorporates low melting point metal fillers such as lead/tin alloys.⁴⁰ In order to obtain high-quality brazed joints, parts must be closely fitted, and the base metals exceptionally clean and free of oxides; joint clearances of 3–8 μm are recommended to enhance capillary flow of the molten brazing materials and provide high joint strength.⁴¹ Gold-based alloys, such as gold/silver, were often used as brazing materials. A gold alloy with 25 wt. % (~32 at. %) silver has a melting point of ~1035 °C, approximately 30 °C below that of gold, 1064 °C.⁴² While gold does not oxidize, the alloy does.

Joining is accomplished by placing small beads of the brazing material, positioned with the work pieces, in a charcoal fire; the emitted carbon monoxide serves as a reducing agent to remove oxide layers from both the braze and the metal parts to be joined. The use of a hot charcoal fire to reduce copper ores has been known since ~5000 BC.^{7,39} Flux, such as naturally occurring sodium carbonate [Na_2CO_3], also helped to dissolve oxide layers.^{40,43} Once the braze is melted, the flame is concentrated on the joint using a reed blowpipe (see Figure 12) which causes the molten brazing material to flow by capillary action and form an adhesive interfacial thin film between the surfaces of the metal parts to be joined. The artisan then removes residual traces of flux from the work piece. One of the characteristics of a brazed joint (a beautiful early example is shown in Figure 13) is the fillet of excess brazing alloy around the joint area. The size of the residual fillet is inversely related to the skill of the craftsman.

The first known joining of gold and silver thin films to base substrates, generally copper, that did not involve mercury interfacial layers or brazing was by electroless plating developed by the Moche Indians in the northern highlands of Peru, beginning ~100 BC.⁴⁴ Using minerals available in the local area, they first dissolved gold in a hot aqueous solution of equal parts potassium aluminum sulfate [$\text{KAl}(\text{SO}_4)_2$], potassium nitrate [KNO_3], and salt [NaCl], a process that took



FIG. 12. A photograph of a wall painting found at Thebes in the tomb of the Vizier Rekh-mi-re on the west bank of the Nile River, across from the modern city of Luxor, Egypt, ~800 km south of the Mediterranean Sea. The image, dating from about 1475 BC, depicts a metal worker engaged in brazing at a workshop attached to the nearby Temple of Amun, at Karnak (east bank). He is using a reed tipped with clay for a blowpipe and tongs to hold the parts to be brazed in a charcoal fire in a clay bowl. Adapted from Ref. 40.

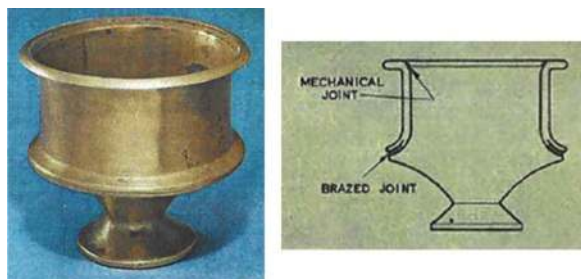
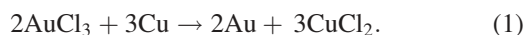


FIG. 13. A photograph of a gold goblet discovered in the Royal Cemetery at Ur (an important Sumerian city-state in ancient Mesopotamia, located at the site of the present-day Iraqi city Tell el-Mugayyar, near the Euphrates River) in the tomb of Queen Pu-abi. It dates to approximately 2500 BC. The construction is quite remarkable; the upper portion is double walled with a brazed joint (the brazing fillet is visible) to the bottom of the cup as shown in the sketch. The goblet is now in the British Museum (London, England). Adapted from Ref. 40.

several days. The solution was then buffered with sodium bicarbonate [NaHCO_3] to form a weakly alkaline solution ($\text{pH} \sim 9$) which was allowed to boil for several minutes before immersing the copper artifact to be plated. The overall reaction is



Metallographic studies of Moche artifacts, coated with gold films whose thicknesses ranged from 2000 \AA to $1 \mu\text{m}$, exhibit evidence of post-deposition heat treatment (annealing) to obtain a film/substrate interdiffusion zone, presumably for better adhesion. An excellent example of craftsmanship is depicted in Figure 14.

III. TRANSFORMATIONAL ADVANCES IN VACUUM TECHNOLOGY, ELECTRONICS, CRYSTALLOGRAPHY, AND SURFACE SCIENCE NECESSARY FOR USHERING IN THE SECOND GOLDEN AGE OF THIN FILMS

A. Vacuum technology: Mechanical pumps

While solution chemistry played an important role in the development of inorganic thin film technology (although not nearly as central as for organic films),⁴⁵ the development of vacuum technology (from the Latin *vacuus*, meaning empty space), starting in the mid-1600s, was essential for providing



FIG. 14. An electroless gold-plated copper mask discovered near Lorna Negra (northern Peru, close to the Ecuadorian border). Adapted from Ref. 44.

cleaner deposition environments necessary for the evolution of surface and thin film science. A critical step in placing the study of vacuum in the forefront of scientific interest was provided by Evangelista Torricelli (1608–1647), an Italian physicist and mathematician who, in ~ 1640 , invented the barometer to measure atmospheric pressure.⁴⁶ (The modern pressure unit Torr is in honor of Torricelli.) His initial experiments were carried out with an $\sim 100 \text{ cm}$ long glass tube, open at one end, filled with liquid mercury, and tightly closed with a fingertip. The tube was then inverted, partially immersed in a mercury reservoir, and the fingertip removed from the tube opening. Some of the mercury flowed out of the tube leaving space at the top such that the height of the liquid column corresponded to the ambient atmospheric pressure.

The empty volume at the top of the barometer was “Torricelli’s void;” he had produced a vacuum! This finding added grist to the long-standing philosophical argument of whether empty volume was possible. The origin of the argument has been ascribed to Aristotle ($\sim 384\text{--}322 \text{ BC}$) who posited that nature cannot contain vacuum because the denser surrounding material would immediately fill the rarefied void.⁴⁷ The theory was supported and restated by Galileo Galilei (1564–1642) based upon an erroneous interpretation of his own 1630 observations involving pumping water uphill.⁴⁶

In 1652, Otto von Guericke (1602–1686) of Magdeburg, Germany, a scientist, inventor, and politician, developed a mechanical piston pump that achieved a vacuum of $\sim 2 \text{ Torr}$.^{48,49} (For comparison, a typical vacuum cleaner produces enough suction to reduce standard atmospheric pressure, 760 Torr , to $\sim 610 \text{ Torr}$.)⁵⁰ von Guericke’s third-generation vacuum system, a model of which is shown in Figure 15,⁵¹ consisted of a bell jar separated from the piston

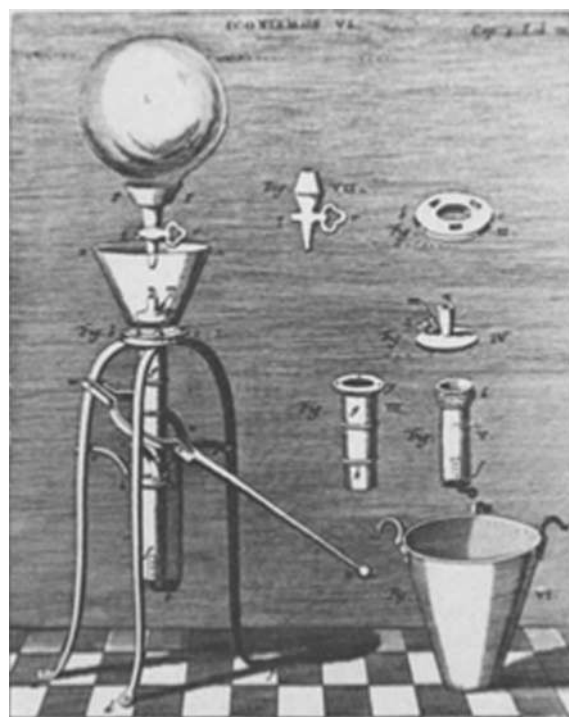


FIG. 15. A model of an early mechanical piston pump developed by Otto von Guericke in ~ 1652 . Adapted from Ref. 51.

pump by a cylinder with a stop-cock. The pump was equipped with two valves near the entrance to the nozzle extending into the bottom of the bell jar, the first valve was located between the nozzle and the cylinder and the second valve between the cylinder and atmosphere. During the piston down-stroke, valve one is closed to stop air from entering the nozzle and bell jar, while valve two is forced open by the air displaced from the cylinder. During the piston return-stroke, valve two is closed, and valve one is forced open by the pressure of the remaining air in the bell jar and nozzle. The percentage pressure decrease per complete piston stroke diminishes continuously as the bell jar pressure is reduced toward the base pressure.

von Guericke used his piston pump to investigate the properties of vacuum in a long series of experiments, the most famous of which are his public demonstrations in front of Emperor Ferdinand III (Regensburg) in 1654, and later in Magdeburg in 1656 (von Guericke was the Mayor of Magdeburg at the time). For the demonstrations, he employed what are now known as the Magdeburg hemispheres (Figure 16),^{49,52,53} ~50 cm in diameter and made of copper with mating rims sealed by grease. One of the hemispheres had a connection for attaching von Guericke's pump and a valve to close it off. When the hemispheres were evacuated to their base pressure, and the valve closed, the hose from the pump was detached.⁵⁴ Two teams of horses (15 horses/team in the initial demonstration and eight horses/team at Magdeburg) could not pull the evacuated sphere apart (Figure 16). This experiment, although basically a stunt,⁵⁵ was instrumental in focusing the attention of scientists on the importance of vacuum, while disproving a centuries-long philosophical conundrum: the hypothesis of "*horror vacui*" (nature abhors a vacuum). von Guericke demonstrated that objects are not pulled by vacuum, but are pushed by the pressure of the surrounding fluids (in his case, atmospheric pressure).

While von Guericke was correct in debunking "*horror vacui*," the impulse load of the horses could easily have pulled the hemispheres apart if they had acted in a concerted fashion. This was demonstrated by Mars Hablanian and C. H. Hemeon in a reenactment of the von Guericke experiments in Boston on the occasion of the 30th Anniversary of the American Vacuum Society (AVS) Annual Symposium, 1983. However, Hablanian and Hemeon pointed out that, to be fair, in von Guericke's time, "... Newton's laws were unknown; force and momentum were usually confused and energy considerations in impulse load calculations were not appreciated."⁵⁵



FIG. 16. A cropped view of the Magdeburg hemisphere experiment from a sketch by Gaspar Schott, appearing in his book *Mechanica Hydraulicopneumatica*, Würzburg, Germany (1657). Adapted from Ref. 54.

B. Power supplies: Pulsed to dc

Another requirement for initiating early experiments in thin film deposition was electrical power. von Guericke also played an important role in this field through his development in 1663 of a crude friction-based electrostatic generator which transformed mechanical work into electrical energy.^{56,57} The generator was based on the triboelectric effect (although the term did not exist at the time), in which a material becomes electrically charged ("static electricity") through friction. The concept was known by the ancient Greeks (e.g., rubbing amber on wool) and first recorded by Thales of Miletus (~624–546 BC),⁵⁸ a pre-Socratic Greek philosopher, mathematician, and one of the Seven Sages of Greece.^{59–61} Thales had enormous influence on the development of Greek natural philosophy due, primarily, to his attempts to explain natural phenomena without reference to mythology.^{59,60} According to Bertrand Russell, "Western philosophy begins with Thales."⁶¹

The modern word "electricity," often attributed to William Gilbert (1544–1603),⁶² an English physician and physicist who was instrumental in launching the modern era of electricity and magnetism,⁶³ actually derives from the Greek word for amber, *ēlektron*.⁶⁴ von Guericke's generator consisted of a sulfur ball—fabricated by pouring liquid sulfur into a glass mold, solidifying the sulfur, then breaking the mold—mounted in a wooden cradle and rotated by a hand crank. The counter electrode was von Guericke's hand rubbing the sulfur ball, which accumulated electrostatic charge, to generate electric sparks.⁶⁵

In 1745, the Dutch scientist Pieter van Musschenbroek (1692–1761) of Leiden University (mathematics, philosophy, medicine, and astrology [the latter is closer to theology than science!]) and Ewald Georg von Kleist (1700–1748), a German lawyer, cleric, and physicist, are credited with independently inventing what today is known as the Leiden jar,^{66,67} an early form of the modern capacitor. However, it appears that Professor Musschenbroek obtained the idea for his research from Andreas Cunaeus (1712–1788), a lawyer who often visited Musschenbroek's laboratory. Cunaeus carried out the initial experiments that led to the Leiden jar⁶⁸ while attempting to reproduce even earlier results by Andreas Gordon (1712–1751), a Professor at Erfurt, Germany, and Georg Mattias Bose (1710–1761) at the University of Wittenberg, Germany.⁶⁹ The device accumulates static electricity between electrodes on the inside and outside of a glass jar.

A typical Leiden jar design, after multiple iterations, consisted of a glass jar with metal foil coating both the inner

and outer surfaces, but not reaching the mouth of the jar in order to prevent arcing between the foils. A rod-shaped electrode projected through the top of the jar and was electrically connected to the inner foil. The jar was charged by connecting the rod to an electrostatic generator of the type developed by von Guericke. However, by this time, a glass cylinder had been substituted for the sulfur sphere, woolen cloth or leather strips were used as the counter electrode (rather than the operator's hand), and an insulated collector electrode was added.^{56,69–71}

In order to store charge in Leyden-jar-based batteries, the glass cylinder of an electrostatic generator was rotated, via a hand crank, against a leather (or wool) strip pressing on the glass. The friction resulted in positive charge accumulating on the leather and negative charge (electrons) on the glass. The electrons were collected by an insulated [perhaps comb-shaped] metal collector electrode. When sufficient charge built up, a spark jumped from the generator collector to the central collector electrode of a nearby Leyden jar where the charge was stored. Originally, the capacitance of the device was measured in units of the number of “jars” of a given size, or by the total area covered with metal. A typical Leyden jar of ~ 0.5 l had a capacitance of about 1 nF.⁷² Daniel Gralath (1708–1767), physicist (founder of the Danzig Research Society) and Mayor of Danzig, Poland, repeated the Leyden jar experiments and was the first to combine several jars, connected in parallel (see Figure 17), to increase the total stored charge.⁷³ The term “battery” was reputedly coined by Benjamin Franklin (1706–1790),⁷⁴ who likened the group of jars to a battery of cannon. The primary limitation of Leyden jar batteries is that they only provide pulsed power, rather than continuous dc power.



FIG. 17. A “battery” consisting of four water-filled Leyden jars. Photograph attributed to Leidse Flessen Museum Boerhave, Leiden, the Netherlands, licensed under the Creative Commons Attribution-Share Alike 3.0 Unported.

The invention of the modern electrochemical battery to provide low-voltage dc power is generally attributed to Count Alessandro Volta (1745–1827), Professor of Natural Philosophy at the University of Pavia, Italy, based upon his work in the 1790s resulting in a classic paper published first in French,⁷⁵ then in English,⁷⁶ in 1800. However, as is often the case in science, others were working in this field much earlier. In 1752, the Swiss scientist Johann Georg Sulzer (1720–1779) placed the tips of two different metals, whose opposite ends were in contact, against his tongue. He reported, “a pungent sensation, reminds me of the taste of green vitriol when I placed my tongue between these metals.” He had unknowingly created a galvanic cell in which his saliva served as the electrolyte carrying current between two dissimilar metal electrodes.⁷⁷ The invention of the galvanic cell is credited to Luigi Galvani (1737–1798), Professor of Anatomy at the University of Bologna, Italy. Galvani reported in 1791 (Ref. 78) that when he touched copper and zinc wires to the leg of a frog, it contracted. He incorrectly explained this in terms of “animal electricity.”⁷⁹ Volta originally appeared to agree with this interpretation, but later refuted the idea⁸⁰ and argued that the frog tissue was merely a conductor (an electrolyte) and that the current caused the animal to respond.⁸¹

The disagreement with Galvani did, however, focus Volta on the study of what today is termed electrochemistry. He replaced the frog's leg with pieces of cloth saturated in brine, which served as the electrolyte between dissimilar metals.⁸² He quickly discovered that larger voltages are obtained from a stack consisting of several pairs of different metal discs, each pair separated by an electrolyte, connected in series to form a “voltaic pile.” The initial metals used were copper and zinc, but Volta found, using an electrometer, that silver and zinc produce a larger electromotive force, a term Volta introduced in 1796.⁸³ Figures 18(a) and 18(b) are an illustration and a photograph, respectively, of an early voltaic pile. Such devices could only provide a few volts; obtaining larger potentials required a series (i.e., a “battery”) of voltaic piles. An example of a small double voltaic pile is shown in Figure 18(c).⁷⁶ In 1801, Volta was invited to Paris where he presented a series of lectures on his voltaic pile battery at the National Institute of France (later to become the Academy of Sciences). Napoleon, the French head of state at the time, was so impressed with Volta that he made him a Count.⁸²

Immediately upon learning of Volta's discovery, William Nicholson (1753–1815), an English scientist, and Anthony Carlisle (1768–1840), surgeon, constructed the first voltaic pile in England—initially with 36 pairs of silver half crowns and zinc discs,⁸⁴ then 100 pairs⁸⁵—and used it for experiments leading to the important discovery of the electrolysis of water.^{86,87} They filled a small glass tube with water, sealed it, and inserted platinum wires which were connected to the terminals of the voltaic battery. As the free ends of the wires were slowly moved toward each other, they observed streams of bubbles produced from each wire. Nicholson and Carlisle demonstrated, by collecting and analyzing the gases, that hydrogen [H_2] evolved from near the cathode and oxygen [O_2] from around the anode “in the ratio of two volumes of H_2 for every volume of O_2 .”^{87,88}

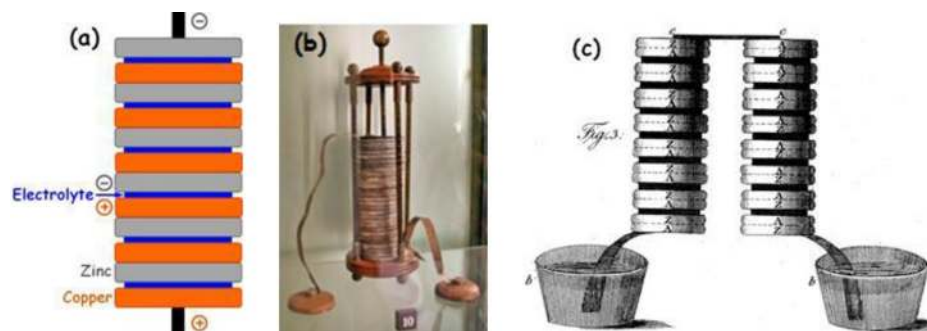


FIG. 18. (a) Schematic illustration of a voltaic pile. (b) Photograph, attributed to GuidoB and licensed under the Creative Commons Attribution-Share Alike 3.0 Unported, of a single voltaic pile. The battery is on display at the Tempio Voltiano Museum, Como, Italy. (c) Sketch of a double voltaic pile consisting of two sets of eight pairs of silver and zinc plates. Adapted from Ref. 76.

A practical problem with voltaic piles, especially with larger ones used to obtain higher voltages, is that the weight of the discs squeezes electrolyte out of the cloths. In 1801, William Cruickshank (1745–1810), a surgeon and Professor of Chemistry at the Royal Military Academy, Woolwich (southeast London), solved this problem and designed the first electric battery for mass production.⁸⁹ In the initial version, Cruickshank arranged 60 pairs of equal-sized zinc and silver sheets cemented together with rosin and beeswax in a long resin-insulated rectangular wooden box, Figure 19, such that all zinc sheets faced one direction and all silver sheets the other. Grooves in the box held the metal plates in position, and the sealed box was filled with an electrolyte of brine, or dilute ammonium chloride $[\text{NH}_4\text{Cl}]$ which has higher conductivity.

In 1836, John Frederic Daniell (1790–1845), first Professor of Chemistry at the newly founded King's College, London, was searching for a way to eliminate hydrogen bubble production in voltaic pile batteries; his solution was to use a second, and insoluble, electrolyte to consume the hydrogen produced by the first.^{91,92} The Daniell battery had a much longer lifetime and was a great improvement over the existing technology. For this contribution, the Royal Society awarded him the Copley Medal in 1836.

Grove (1811–1896), who in 1852 published the first paper on sputter deposition and ion etching (Sec. IV B 1), was—like many scientists of his time—interested in electricity. In 1839, he constructed his own version of Daniell's two-fluid voltaic cell, consisting of a platinum cathode immersed in concentrated nitric acid and a zinc anode in dilute sulfuric acid.⁹³ A single cell delivered approximately 2 V, much higher than other contemporary single-cell

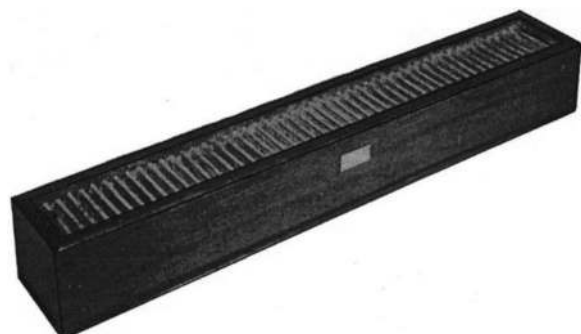


FIG. 19. Photograph, courtesy of Brian Bowers, of a restored Cruickshank trough voltaic pile battery, 1801. Adapted from Ref. 90. The trough is on display at the Royal Institution, London, England.

batteries. As a postscript to his electrochemical battery paper, Grove also described a “gaseous voltaic battery,” with cells connected in series. Each cell contained two glass tubes, one with oxygen and one with hydrogen, the open ends of which were immersed in dilute sulfuric acid. Both tubes had platinum electrodes. An illustration of the key features of this battery from a later publication,⁹⁴ in which he describes the gas cell more clearly, is shown in Figure 20. Grove provides the following explanation.

“In the Philosophical Magazine for December 1842 I have published an account of a voltaic battery in which the active ingredients were gases, and by which the decomposition of water was effected by means of its composition. The battery described in that paper.... consisted of a series of tubes containing strips of platinum foil covered with a pulverulent deposit of the same metal; the platinum passed through the upper parts of the tubes, which were closed with cement, the lower extremities were open; they were arranged in pairs in separate vessels of dilute sulphuric acid, and of each pair one tube was charged with oxygen, the other with hydrogen gas, in quantities such as would allow the platinum to touch the dilute acid; the platinum in the oxygen of one pair was metallically connected with the platinum in the hydrogen of the next, and a voltaic series of 50 pairs was thus formed.”

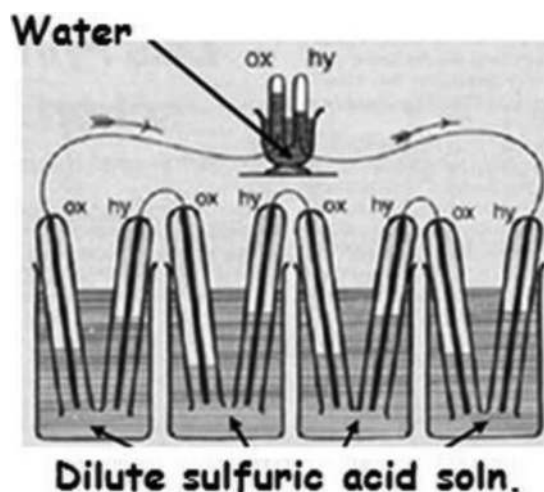
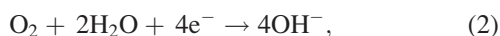


FIG. 20. A sketch of Groves' “gaseous voltaic battery.” Adapted from Ref. 94. The dark black line in each tube represents a platinum electrode.

Additional results obtained using the gas voltaic battery are discussed in Ref. 95 and a simpler design provided in Ref. 96. For his discovery, Grove received the Medal of the Royal Society in 1847 and in his Bakerian Lecture, “On Certain Phenomena of Voltaic Ignition and the Decomposition of Water into its Constituent Gases by Heat,” to the Society on November 19, 1846, he also demonstrated catalysis, showing that steam in contact with a hot platinum surface is catalytically dissociated to hydrogen and oxygen. In addition, Grove used a platinum-filament electric light, powered by his “two-fluid” Pt/Zn battery, to illuminate the lecture theater (like von Guerke, Sec. III A, he was both a scientist and a stuntman).⁹⁷ This was a year before Thomas Edison (1847–1931), who later developed a commercial carbon-filament light bulb,⁹⁸ was born. The modern rare-gas-filled tungsten-filament incandescent light bulb was developed by Irving Langmuir (1881–1957), at General Electric Research Laboratories, Schenectady, New York, and patented in 1916.^{45,99}

Grove’s gas voltaic battery was also the first fuel cell, although that term, introduced by Ludwig Mond and Carl Langer in 1889,¹⁰⁰ was still 50 years into the future. In Grove’s experiments, power was produced by the electrochemical oxidation of hydrogen (the fuel) to form water. At the platinum electrode in oxygen



while at the platinum electrode in hydrogen



The OH^- hydroxyl ions react in the conducting electrolyte with H^+ ions to produce H_2O and thus generate a voltage. Current is obtained as electrons [e^-] flow through the external circuit from the anode (the electrode where hydrogen ions are produced) to the cathodic counter electrode. Grove also showed that carbon monoxide [CO], hydrocarbons (ethylene [C_2H_4] and ethane [C_2H_6]), and solid sources (sulfur and phosphorus) can serve as the fuel for O_2 oxidation.⁹⁶ Groves classic book, *On the Correlation of Physical Forces*,⁹⁶ contains, in addition to further discussion of his fuel cell, the first clear statement of energy conservation (i.e., the first law of thermodynamics).

C. Crystallography and Miller indices

Yet another important contribution, which proved to be essential for the budding field of thin films, was the development of crystallography, the evolution of which is complex,

multifarious, and fascinating in its own right. Plato (428–348 BC), a Greek philosopher/mathematician, describes in *Timaeus* (~360 BC),¹⁰¹ one of his famous 36 teaching dialogues, the set of five (and only five) regular congruent convex polyhedra—known from ancient times—with equivalent faces composed of congruent convex regular polygons (see Figure 21). He assumed them to be the fundamental building blocks of nature; that is, the shapes represent the “elements” known at the time. The tetrahedron with sharp points is fire, the regular cube is earth, the smooth octahedron is air, the dodecahedron represents stars and planets, and the rounded and flowing icosahedron is water. While the five Platonic solids do not, other than the cube, correspond to Bravais crystal lattices, they do represent some prominent crystal and nanocrystalline habits. Early crystallographers were aware of them as well the Archimedean (287–212 BC) solid shapes.¹⁰²

Johannes Kepler (1571–1630), a German mathematician and astronomer, was fascinated that snowflakes have six corners (6-fold symmetry) and in 1611 wrote *Strena Seu de Nive Sexangulain* (*Six-cornered Snowflake*)¹⁰³ in which he gave the first mathematical description of crystals. He reasoned (not entirely correctly since he knew nothing about atomic structure) that snowflakes have six corners since hexagons, like squares and triangles, are space filling. He describes, using spheres, close-packed hexagonal and less dense simple-cubic crystal structures. Kepler’s interest in packing density (“Kepler’s conjecture”) came from discussions with a friend, Thomas Harriot (an English mathematician), who was a navigator for Walter Raleigh’s “new world” voyages and was given the task of how best to stack cannonballs.¹⁰⁴

A Danish Catholic Bishop with an interest in science, Nicolas Steno [Niels Stensen in Danish] (1638–1686), showed that the angles between corresponding faces of trigonal quartz [SiO_2] crystals, irrespective of size or morphology, are the same (Steno’s Law).¹⁰⁵ Moritz Anton Capperer (1685–1769), a Swiss physician with a passion for mineralogy, expanded Steno’s Law and noted that each mineral crystal has its own characteristic set of interfacial angles (1723).¹⁰⁶ He also appears to be the first to have used the word crystallography in print. Jean-Baptiste Louis Romé de l’Isle (1736–1790), a French mineralogist, is best known for his *Essai de Cristallographie* (1772), and a second edition published in 1783 as *Cristallographie*, in which he built on the earlier work of Steno and Capperer to formulate the Law of Constancy of Interfacial Angles.¹⁰⁷ A Professor of Chemistry and Mineralogy at Uppsala University, Torbern Olof Bergmann (1735–1784), an elected member of the

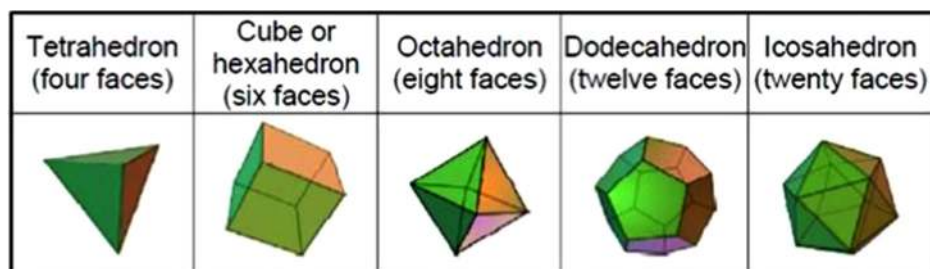


FIG. 21. The five Platonic solids. Drawing attributed to DTR and licensed under the Creative Commons Attribution-Share Alike 3.0 Unported.

Royal Swedish Academy of Sciences and Fellow of the Royal Society of London, demonstrated on paper that rhombohedral calcium carbonate [CaCO_3] crystals can be constructed from smaller rhombohedral units. Similarly, rock salt [NaCl] crystals can be constructed from small cubes.¹⁰⁸

René-Just Haüy¹⁰⁹ (1743–1822) was an ordained priest and Professor of Literature at the Collège du Cardinal Lemoine in Paris who developed an interest in mineralogy after having attended lectures by Louis-Jean-Marie Daubenton (1716–1799), a famous French naturalist. The story goes that Haüy's fascination with the crystalline structure of minerals was sparked when, upon examining an excellent calcium carbonate [CaCO_3] specimen belonging to a friend, he dropped it and the crystal shattered [cleaved] into small rhombohedrons. He examined the fragments and was struck by their geometric forms. It is likely that Haüy knew of the prior work of Bergmann, and perhaps that of Steno and Cappeler.

Haüy, in his 1784 *Essai d'une Théorie sur la Structure des Crystaux*,¹¹⁰ collected earlier advances in crystallography, together with his more recent results, into a single coherent theory based on the idea that crystals are composed of fundamental structural units, the “molécules constitutives” (later renamed by him as “molécules intégrantes”). From this, he reasoned that the slope of each macroscopic crystal face must be mathematically related to the shapes of the fundamental structure and describable by integers corresponding to the number of units constituting the “rise over run” ratio of that face. That is, Haüy's “Law of Rational Indices,” the forerunner of modern Miller indices,¹¹¹ states that each crystal face can be described by a set of small integer numbers (Figure 22).

For his work, Haüy was elected to the Paris Academy of Science in 1783. After nearly being executed during the French revolution for refusing to swear an oath of allegiance to the new regime, he was appointed as a Professor of

Physics and Mineralogy at the École des Mines in 1795, and later became Professor of Mineralogy at the Muséum d'Histoire Naturelle. Haüy, in 1801, produced an extraordinarily comprehensive four-volume treatise cataloging, with an atlas of figures, all minerals known at the time.¹¹² In 1809, Haüy also assumed the newly created Chair of Mineralogy at the Sorbonne. He retained both posts until his death. He is today considered by many biographers to be the father of crystallography.¹⁰⁹

A quote from Haüy's *Traité de Minéralogie* provides interesting insights into his analytical reasoning skills¹¹³ long before the availability of what are today common experimental mineralogical structural probes such as x-ray diffraction and transmission electron microscopy.

“The polyhedral forms of which it might seem a directing hand had shaped the outlines and angles, with the assistance of a compass; the variations that these forms undergo in the same substance, without losing their regularity,... The carbonate of lime, for example, takes according to circumstances the form of a rhombohedron, that of a regular hexagonal prism, that of a solid terminated by twelve scalenohedral triangles, that of a dodecahedron with pentagonal faces (rhombohedron and hexagonal prism), etc. The sulfide of iron or pyrite produces now cubes, now regular octahedrons, here dodecahedrons with pentagonal faces (pyritohedrons), there icosahedrons with triangular faces (pyritohedron and octahedron)... To illustrate with one example let one place by the side of a hexagonal prism of calcite the dodecahedron with scalene faces [scalenohedron], it would be difficult for anyone to imagine how two polyhedrons, so contrasted at first inspection, should unite, and, so to speak, lose themselves, in the crystallization of the same mineral.”

Christian Samuel Weiss (1780–1856) and William Hallowes Miller (1801–1880), both mineralogists, further extended crystallography into the modern era. Weiss, a Professor of Mineralogy at the University of Berlin, followed the work of Haüy, corrected some misconceptions and, most importantly, placed crystallography on a more mathematical basis, defining crystal faces and directions in terms of fundamental crystal axes. He also developed the concept of crystallographic zones (the Weiss zone law), each defined by a set of crystal faces which are parallel to a common crystal axis.¹¹⁴ William Hallowes Miller (1801–1880) was educated at Cambridge and became Professor of Mineralogy in 1832.¹¹¹ While his early work was in hydrodynamics, he became interested in crystallography and published his most famous work, *Treatise on Crystallography*, in 1839.¹¹⁵

Miller took Weiss' system for representing crystal planes and directions one step further, resulting in the present system in which any crystal plane or direction can be related to the crystal axes by sets of three integers hkl , the Miller indices, defined along the x , y , and z axes.¹¹⁴ Figure 23 is an example showing a few high-symmetry directions, represented as $[hkl]$, and planes (hkl) , associated with the unit cell of a simple cubic crystal whose sides are of

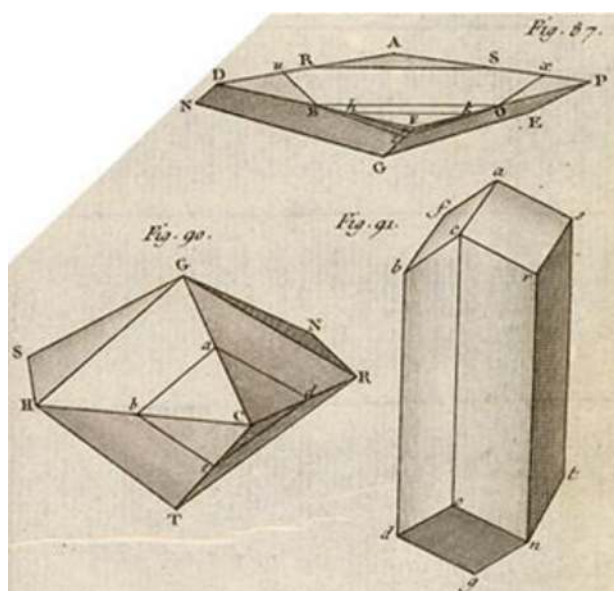


FIG. 22. Drawings of crystal structures, with planes labeled, from a 1784 book by René-Just Haüy, the “father of crystallography.” Adapted from Ref. 110.

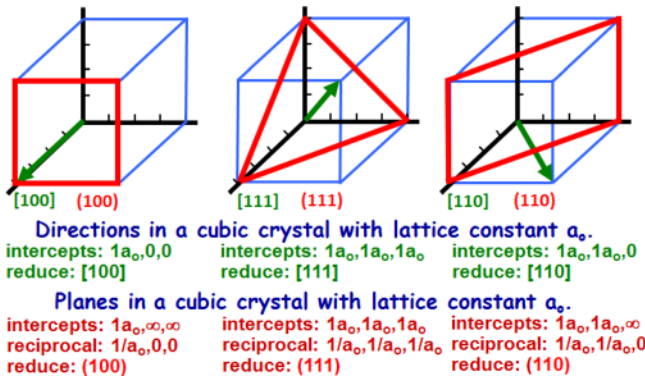


FIG. 23. Three high-symmetry crystal directions, indicated by arrows in green, with planes in red, are shown for the unit cell, the fundamental building block, of a simple cubic crystal. Rules for determining the Miller index representation of the $[hkl]$ directions and (hkl) planes (see text for definitions) are listed below the unit cells. For example, to find the Miller indices of the front plane (outlined in red) of the unit cube, first determine the intercepts of the plane, which are a_0 , ∞ , and ∞ . Next, take the reciprocal of the intercepts, which yields $1/a_0$, 0, and 0. Finally, reduce the results to the lowest set of integers by multiplying each reciprocal intercept by its unit cell dimension (in the simple case of a cube, the lengths in x , y , and z are all a_0). Thus, the plane is (100), written by convention with no commas.

length a_0 (the “lattice parameter”). The front face (outlined in red) of the left cube, one unit distance a_0 along the x -axis, is the (100) plane, which is a member of the $\{100\}$ family of six planes related by symmetry. For example, the plane comprising the right side of the cube, positioned a_0 along the y axis, is labeled (010) and the top plane of the cube is (001). The remaining three planes in the $\{100\}$ family are represented with minus signs; the rear face is $(\bar{1}00)$, the left side is $(0\bar{1}0)$, and the cube bottom is $(00\bar{1})$. Note from Figure 23 that for cubic crystals, the direction $[hkl]$ is orthogonal to the corresponding (hkl) plane, a fact easily proven by geometry as well as by inspection. Miller indices are very powerful for easily determining and specifying crystallographic information. For example, the spacing d_{hkl} between the closest parallel (hkl) planes of a cubic crystal is simply given by

$$d_{hkl} = a_0 / (h^2 + k^2 + l^2)^{1/2}. \quad (4)$$

Thus, for the (100) plane shown here, $d_{100} = a_0$, the distance between the front and back planes of the cube. While this is obvious for cubic crystals, similar geometric relationships allow equally rapid determinations of crystal relationships in complex crystals exhibiting much less symmetry.

D. Surface science and thin film nucleation

Another essential development was provided by Thomas Young (1773–1829), an English scientist who made important contributions in a variety of areas including early work in deciphering the hieroglyphic text inscribed on the Egyptian Rosetta Stone (King Plotemy V, Memphis, 196 BC).^{116,117} In 1805, Young published an equation,¹¹⁸ which now bears his name, that forms the basis for much of surface science. Young’s equation describes the wetting angle of a liquid droplet on a solid substrate in terms of surface and interfacial energies per unit area; this is also the starting point for the physical chemistry description of the heterogeneous capillarity model of thin film nucleation.¹¹⁹ The equation states

$$\gamma_{s-v} = \gamma_{l-v} \cos \theta + \gamma_{s-l}, \quad (5)$$

where γ_{s-v} is the solid-vapor surface tension, γ_{l-v} is the liquid-vapor surface tension, γ_{s-l} is the solid-liquid interfacial energy per unit area, and θ is the droplet wetting angle (the angle between the solid-liquid and the liquid-vapor interfaces). The surface tension terms γ , expressed as vectors, and the wetting angle θ are defined geometrically in the center illustration of Figure 24(a).

The left image in Figure 24(a) represents perfect wetting: $\theta = 0$ and $\gamma_{s-v} = (\gamma_{l-v} + \gamma_{s-l})$, corresponding to a strong solid-liquid interaction. The two figures on the right side of Figure 24(a) illustrate poor wetting and no wetting, respectively: weak solid-liquid interactions. If the liquid droplet is

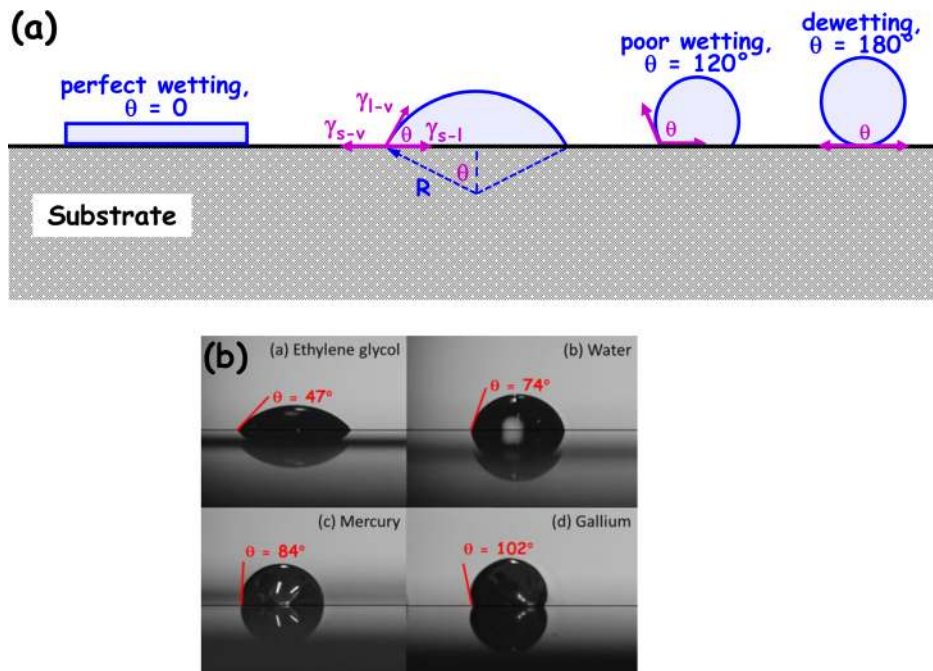


FIG. 24. (a) Schematic illustrations of wetting interactions for different liquid droplets on a solid surface. γ_{s-v} is the solid-vapor surface tension, γ_{l-v} is the liquid-vapor surface tension, γ_{s-l} is the solid-liquid interfacial energy per unit area, and θ is the droplet wetting angle. See text for further explanation. (b) Photographs showing measured wetting angles θ for four different liquid droplets on solid selenium. Measurements for ethylene glycol $[C_2H_4(OH)_2]$ and water were carried out at room temperature and mercury is liquid at room temperature and gallium at $30^\circ C$ (for the Ga experiment, the selenium substrate was heated to $40^\circ C$). The black line indicates the solid-liquid interface. Figure 24(b) is adapted from Ref. 120.

water, perfect wetting and dewetting correspond to superhydrophilic (“layer-by-layer” growth in the language of thin film deposition) and superhydrophobic interactions. In fact, in the limit, neither extreme is possible and θ varies from small values for strong interactions (rain drops spread out on a rusty car) to large values for weak interactions (rain drops ball up on a freshly waxed car). Recent wetting angle measurements for droplets of four different liquids on solid selenium are shown in Figure 24(b).¹²⁰

A zeroth-order application of the concepts of surface wetting to a simplified thermodynamic model of heterogeneous nucleation is illustrated in Figure 25 where the blue hemispherical cap represents an incipient solid nucleus on, for example, an amorphous solid substrate (if the substrate were crystalline, the substrate surface symmetry would act as an atomic-scale template in determining the island shape). Assume that the nucleus, formed by vapor phase deposition, has a mean dimension r and contact angle θ with the substrate. The surface area of the nucleus is $a_1 r^2$, the contact area is $a_2 r^2$, and the volume is $a_3 r^3$, where the a_i coefficients are constants of geometry ($a_1 = 2\pi(1 - \cos\theta)$, $a_2 = \pi(\sin^2\theta)$, and $a_3 = 1/3\pi(2 - 3\cos\theta + \cos^3\theta)$). Thus, the total free energy of the nucleus with respect to dissociation into the vapor phase is¹¹⁹

$$\Delta G = a_1 r^2 \gamma_{f-v} + a_2 r^2 \gamma_{s-f} - a_2 r^2 \gamma_{s-v} + a_3 r^3 \Delta G_V, \quad (6)$$

for which ΔG_V is the (negative) Gibbs free energy per unit volume for the phase transition from the gas to the solid.

Since the first three terms in Eq. (6) vary as r^2 and the last term, an energy gain at deposition temperatures for which the solid phase (rather than the gas) is in equilibrium, varies as r^3 , there must exist a critical nucleus size r^* . If the deposition rate is high enough and the growth temperature is low enough, local density fluctuations in the two-dimensional atom gas on the substrate surface will give rise to sufficiently large local spreading pressures to form stable clusters with $r > r^*$; that is, clusters which have a higher probability to grow than to dissociate. r^* is easily obtained by differentiating equation (6) and setting it equal to zero

$$r^* = -2(a_1 \gamma_{f-v} + a_2 \gamma_{s-f} - a_2 \gamma_{s-v}) / 3a_3 \Delta G_V \quad (7)$$

$$r^* \propto \langle \gamma \rangle / \Delta G_V.$$

Thus, the critical island size is proportional to an average surface energy cost per unit area $\langle \gamma \rangle$ divided by the energy gain, the Gibbs free energy per unit volume ΔG_V of the gas/solid phase transition.

Starting with the first and second laws of thermodynamics, it is easy to show that for vapor-phase film growth, ΔG_V can be expressed as¹¹⁹

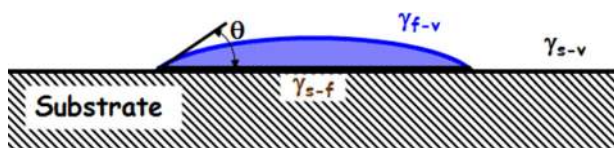


FIG. 25. Schematic illustration of a hemispherical-cap shaped nucleus on a solid substrate. The γ terms are interfacial energies per unit area (i.e., surface tensions) and the subscripts s, f, and v represent the substrate, film, and vapor phases. Adapted from Ref. 119.

$$\Delta G_V \propto kT_s \ln(J_i/J_e), \quad (8)$$

where k is Boltzmann’s constant, T_s is the substrate temperature, J_i is the atom flux incident at the substrate, and J_e is the desorbing flux equivalent to the equilibrium vapor pressure of the deposited species at T_s . Substituting Eq. (8) into (7) yields the parametric relationship

$$r^* \propto \langle \gamma \rangle / kT_s \ln(J_i/J_e). \quad (9)$$

The model is quite crude and does not include, among other things, the size dependence of γ and J_e (typical critical nuclei sizes are only a few atoms). More sophisticated kinetic, rather than thermodynamic, models are available.^{119,121} Nevertheless, the simple thermodynamic model captures much of the essential physics of the process and is consistent with the general behavior of nucleation and the early stages of film growth. As one example, Eq. (9) correctly predicts that r^* increases with film deposition temperature due to the faster than exponential T_s dependence of J_e . Clearly, in the limit of very high substrate temperature, $r^* \rightarrow \infty$, nucleation is not possible, and the gas phase is more stable than the solid.

E. Vacuum technology again: The mercury pump and the McLeod gauge

Much better vacuum was required in order for scientists in the 1800s to make progress in the study of thin film growth from the vapor-phase. This was solved by a German chemist, Hermann Sprengel (1834–1906), who developed a practical mercury momentum transfer pump in 1865.¹²² The Sprengel pump was an improvement over the original mercury pump invented by Heinrich Geissler (1814–1879), a German glassblower, in 1855.¹²³ The base pressure claimed by Sprengel in his initial publication was $\sim 6 \times 10^{-4}$ Torr, and limited by leaks in vulcanized rubber joints connecting glass tubes (the rubber tubing was cemented to the glass and the joints were bound with copper wire). While lower pressures were achieved with later versions of the pump,¹²⁴ pressures of 10^{-3} – 10^{-4} Torr are sufficient to provide ballistic environments (i.e., gas atom mean free paths of the order of, or larger than, system dimensions) for investigating gas discharges, evaporation, and sputtering in the small evacuated chambers of that era.

Sprengel’s pump was essential for the development of practical incandescent carbon-filament-based light bulbs by Thomas Edison (1847–1931), who was issued a U.S. patent for an “Electric Lamp” in 1880.⁹⁸ It should be noted, however, that the history of the light bulb is rich and interesting; it involves many previous researchers stretching back to at least 1802 as chronicled in Ref. 125. Edison did not “invent” the light bulb, he took advantage of the availability of better vacuum to develop a much longer-lived bulb which was commercially viable.

An initial prototype of the Sprengel mercury pump is shown in Figure 26(a).¹²² Droplets of mercury (a heavy metal which is liquid at room temperature), falling through a small-diameter (2.50–2.75 mm) glass tube, trap and compress air by momentum transfer. The tube, labeled cd in

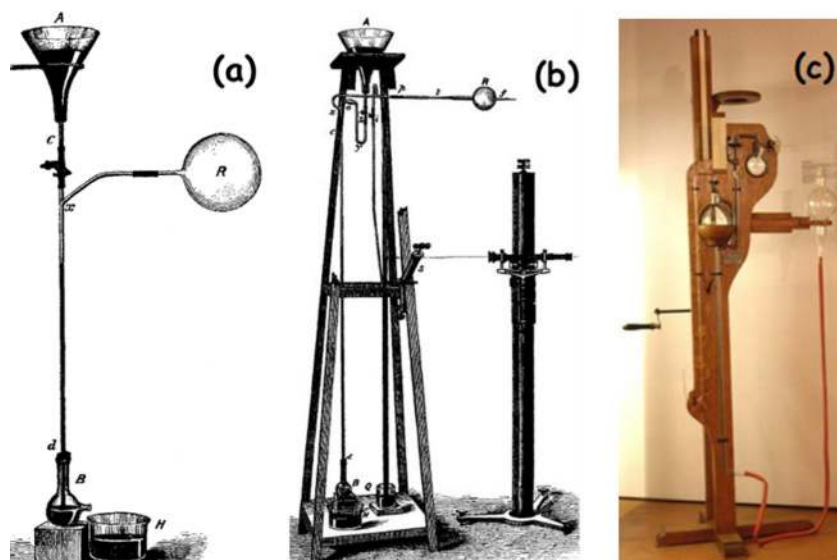


FIG. 26. Drawings of (a) a prototype and (b) an initial version of Sprengel's mercury transfer pump. Adapted from Ref. 122. (c) A later version of the pump, presently housed in the Dr. Guislain Museum, Ghent, Belgium. Photograph courtesy of Luca Borghi for Himetop, The History of Medicine Topographical Database.

Figure 26(a), was ~ 76 cm long and extended from the funnel A to enter the glass bulb B through a vulcanized-rubber stopper. The bulb has a spout several mm above the lower end of tube cd.

In operation, mercury was added to the funnel A, and the stopcock at c opened allowing mercury droplets to fall, trap air, and reduce the pressure in chamber R. Air and mercury were exhausted through the spout of bulb B. The mercury collected in basin H was poured back into funnel A for continued pumping. The second version of the pump, described in the same paper,¹²² is shown in Figure 26(b). It was approximately 1.8 m tall and Sprengel reported using 4.5 to 6.8 kg of mercury during operation. The pump contained a mercury pressure gauge attached to the evacuated chamber and a mechanical piston backing pump S. Later versions incorporated continuous mercury recycling. With the combination of the mechanical and mercury pumps, a 0.5 liter chamber could be evacuated in ≥ 20 min. The importance of Sprengel's work was recognized by the Royal Society of London who elected him as a Fellow in 1878.

Improvements in vacuum technology required better gauging in order to measure the increasingly lower pressures produced. In 1874, Herbert McLeod (1841–1923), a British chemist, developed what today is termed the McLeod gauge^{126,127} which operates based upon Boyle's law. Robert Boyle (1627–1691), another British chemist, showed in 1662 that for a closed system at constant temperature, the product of the pressure P and volume V remains constant.¹²⁸ McLeod designed the gauge "for estimating the pressure of a gas when its tension is so low that indications of a barometer and an accurate cathetometer [an instrument for measuring vertical distances; it consists of an accurately graduated scale and a horizontal telescope capable of being moved up and down a rigid vertical column] cannot safely be relied on, unless indeed a very wide barometer and an accurate cathetometer be employed. The method consists in condensing a known volume of the gas into a smaller space [using liquid mercury] and measuring its tension under the new conditions."¹²⁹ In operation, the gauge compresses a known volume V_1 of the gas at the unknown system pressure P_1 to a

much smaller volume V_2 in a mercury manometer from which pressure P_2 can be determined.¹³⁰ Thus, by Boyle's law, the system pressure $P_1 = P_2 V_2 / V_1$.

An illustration of the essential features of a McLeod gauge is shown in Figure 27. The gauge volume V_1 is initially equilibrated to the unknown vacuum system pressure P_1 to be measured. V_1 in Figure 27 is the total volume of the reservoir plus the closed calibrated tube above it; that is $V_1 = V + A \cdot h_0$. The pressure in the gauge is then compressed to P_2 , in a smaller volume $V_2 = A \cdot h$, using liquid mercury to partially fill the initial gauge volume. This is commonly done by rotating the gauge to allow mercury inflow from an attached source or, as shown in Figure 27, using a plunger. The difference h between the mercury heights of the closed left and open right tubes, together with the known gauge volume, provides the vacuum system pressure. The advantage of the McLeod gauge is that it is absolute for non-condensable gases. However, condensable gases (water vapor and mechanical pump oil vapor are the usual problems) strongly affect the results. Thus, a cold trap (liquid air

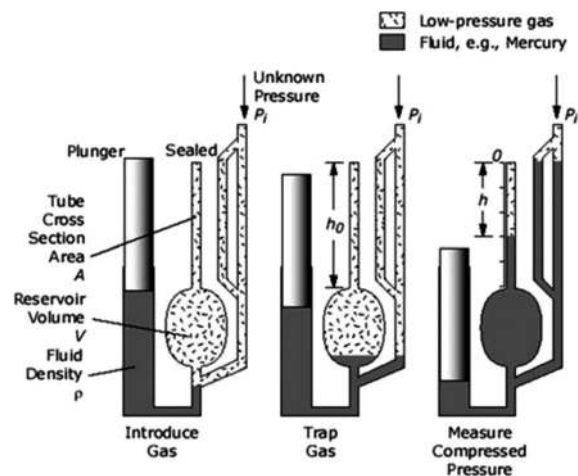


FIG. 27. An illustration showing the essential features of a McLeod gauge for pressure measurements to $\sim 10^{-5}$ Torr. Figure courtesy of eFunda and available at http://www.efunda.com/designstandards/sensors/mcleod/mcleod_intro.cfm.

initially, now liquid nitrogen) is used to remove the condensable gases. McLeod gauges are still in use today, primarily for calibrating other gauges over the pressure range from ~ 1 to 10^{-5} Torr.

IV. THE SECOND GOLDEN AGE OF THIN FILMS: THE LATE 1700s THROUGH THE EARLY 1900s AD

A. Film growth from solution

1. Electrodeposition

By the late 1700s and early 1800s, many of the best minds in science were focused on investigating the growth and properties of thin films. William Nicholson, who with Anthony Carlisle, discovered the electrolysis of water^{86,87} (see Sec. III B), also briefly described electrodeposition of copper in the same 1800 paper in which he discusses his initial experiments with a voltaic pile.⁸⁴ Near the end of the article, he reports that upon moving two copper wires, connected to a voltaic battery, to within 0.85 cm of each other in very dilute hydrochloric acid [HCl] solution: "... the minus wire gave out some hydrogen during an hour, while the plus wire was corroded, and exhibited no oxide; but a deposition of copper was formed round the minus, or lower wire, which began at its lower end and that deposition at the end of four hours formed a ramified metallic vegetation, nine or ten times the bulk of the wire it surrounded." Thus, a very dendritic copper film [the roughness was probably due to contamination] was formed.

William Cruickshank, in the following paper of the same journal issue, also discusses water electrolysis, but again ends by describing electrodeposition.¹³¹

"The tube was filled with a solution of acetate of lead, to which an excess of acid was added to counteract the effects of the alkali. When the communication was made [the circuit completed] in the usual way, no gas could be perceived, but after a minute or two, some fine metallic crystals were perceived at the extremity of the wire. These soon increased, and assumed the form of a feather. The lead thus precipitated was perfectly in its metallic state, and very brilliant. A solution of the sulphate of copper was next employed, and with the same result, the copper being precipitated in its metallic form. The most beautiful precipitate, however, was that of silver from its solution in the nitrous acid. In this case, the metal shot into fine needle-like crystals articulated or joined to each other."

In 1803, Professor Luigi Brugnatelli (1858–1928), a close friend of Alessandro Volta (see Sec. III B) at the University of Pavia, Italy, wrote to a colleague, Jean Baptiste van Mons, Professor of Chemistry at Leuven (Belgium) describing how he had successfully deposited gold films onto silver medals¹³² which served as one electrode in an "ammoniuret of gold" electrolyte. The negative electrode was a voltaic pile battery. The electrolyte, highly explosive, was prepared by adding six parts of "aqueous ammonia" [ammonium hydroxide, $\text{NH}_3(\text{aq})$] to one part saturated

solution of "gold in nitro-muriatic acid" (gold in a mixture of hydrochloric [HCl] and nitric [HNO_3] acids). The historical name for HCl is muriatic acid; the mixture of concentrated HCl and HNO_3 , typically in a molar ratio 1:3, is today termed aqua regia (Latin for royal water). Aqua regia, also called nitro-hydrochloric acid, is a highly corrosive solution with yellow to red fumes.

Nitric acid is a powerful oxidizer which will dissolve a small amount of gold, forming gold ions [Au^{3+}]. The hydrochloric acid provides a supply of chloride ions [Cl^-], which react with the gold ions to produce chloroaurate AuCl_4^- anions, also in solution. Gold ions from solution deposit on the cathode, as chloroaurate ions move toward the anode, allowing further oxidation of gold to take place. Brugnatelli reported that he had "... recently gilt in a perfect manner two large silver medals, by bringing them into communication, by means of a steel wire, with the negative pole of a voltaic pile, and keeping them, one after the other, immersed in ammoniuret of gold newly made and well saturated." Professor van Mons, the editor of a relatively obscure Belgium journal, published Brugnatelli's letter in 1803.¹³³ It was republished in English in a British journal in 1805.¹³⁴ Unfortunately for Brugnatelli, a disagreement with the French Academy of Sciences, the leading scientific body of Europe at the time, prevented the full details of Brugnatelli's work being published and his results remained largely unknown. In fact, George Shaw in his 1842 book, *A Manual of Electrochemistry*,¹³⁵ wrote: "From Brugnatelli to 1830, no experiments were published on the applications of electricity to the deposition of metals for the purpose of art."

The 1817 finding by Joseph von Fraunhofer (1787–1826), a German optician, that antireflective coatings can be produced on glass telescope lenses using concentrated sulfuric acid [H_2SO_4] and HNO_3 to etch and redeposit films, although not electroplating in the usual sense of the term, was very important for progress in optical coatings.¹³⁶

Frederick Daniell's initial publication describing his two-fluid voltaic cell (see Sec. III B) resulted from a letter to Faraday (1791–1867) in which, in addition to the new battery design,⁹¹ he reported electrodeposition of Cu films on large Ag plates when touched with a Zn wire in dilute sulfuric acid "to which a portion of sulphate of copper [CuSO_4] had been added." Warren de la Rue (1815–1889), a British chemist and eldest son of Thomas de La Rue, who founded a company (which still exists) that prints bank notes, constructed a Daniell's cell and used it to deposit copper films on copper; "the copper plate is also covered with a coating of metallic copper which is continually being deposited; and so perfect is the sheet of copper thus formed that, being stripped off, it has the polish and even a counterpart of every scratch of the plate on which it is deposited."¹³⁷

John Wright (1808–1844), a surgeon in Birmingham, the center of the British metal working industry, was experimenting with electricity in the late 1830s. After reading an article by Carl Wilhelm Scheele (1742–1746), a Swedish chemist,¹³⁸ on the behavior of gold and silver cyanides [$\text{Au}(\text{CN})$ and $\text{Ag}(\text{CN})$] in solutions of potassium cyanide [$\text{K}(\text{CN})$], he devised an experiment to test such solutions as

electrolytes.¹³² The results were very promising. He thus contacted the nearby Elkington plating company and convinced them to pay him £300 for the rights to patent the process and a further £500, plus royalties, after the patent was approved. George Richards Elkington (1801–1865) and his cousin Henry Elkington filed for the patent on March 25, 1840. British patent 8447, “Improvements in Coating, Covering, or Plating Certain Metals,” was issued September 25,¹³⁹ 37 years after Brugnatelli’s published his gold plating experiments. The cyanide process became widely used and is still common today. Wright benefited from a steady royalty income.¹³²

2. Sol-gel processing

A sol is a stable suspension of colloidal particles in a liquid. For a sol to exist, the solid particles, denser than the surrounding liquid, must be small enough that the net short-range forces responsible for dispersion (van der Waals, electrostatic, and entropic) are greater than those of gravity. An early example of a sol, Au nanoparticles (~ 200 Å in diameter) in a chloride solution, was produced by Faraday in the mid-1850s.¹⁴⁰ He used phosphorus to reduce a solution of tetrachloroauric acid [HAuCl_4] by a variety of routes; the most successful being the addition of a “drop” of a solution of phosphorus in carbon disulphide [CS_2]. The result was a “beautiful ruby [colored] fluid” such as shown in Figure 28 (see also Fig. 1(a), Ref. 141) from a display at the Royal Institution of Great Britain (London). The red color arises from strong plasmon absorption at ~ 5200 Å, much like that observed in the famous Lycurgus glass cups dating from ~ 350 AD, Rome.¹⁴²

In the sol-gel film formation process, the sol is the precursor for forming a gel, a three-dimensional solid network with trapped liquid (primarily water). Gels are diphasic, containing both liquid and solid phases; the morphology of the solid phase ranges from discrete particles to continuous polymer networks. Films are formed by, for example, dip-coating or spin coating unto a substrate, drying the gel, and annealing (firing) the resulting layer for densification and grain growth.



FIG. 28. Gold (~ 200 Å colloidal crystals) sol produced following the recipe provided by Michael Faraday in the mid-1850s. Adapted from Ref. 140. Figure Courtesy of the Royal Institution of Great Britain/Paul Wilkinson.

Interest in sol-gel processing of inorganic ceramics and glasses began in the 1840s with the investigation of silica gels by Ebelmen^{143–145} and Grahams¹⁴⁶ who observed that the hydrolysis of TEOS, tetraethyl orthosilicate [$\text{Si}(\text{OC}_2\text{H}_5)_4$], under acidic conditions yields SiO_2 in the form of a “glass-like material.”¹⁴⁴ Fibers were drawn from the viscous gel, and monolithic films on optical lenses, as well as composites, were formed.¹⁴⁵ However, extremely long drying times of one year or more were necessary to avoid the silica gels fracturing into a fine powder. Alfonso Cossa synthesized the first alumina gels in 1870;¹⁴⁷ Alfred Stock and Karl Somieski synthesized silazanes [a general term for a hydride of silicon and nitrogen], the precursors to Si_3N_4 .¹⁴⁸

In 1885, Ditte used sol-gel solution growth to form vanadium pentoxide [V_2O_5] films.¹⁴⁹ The layers were synthesized from red vanadium pentoxide sols produced by heating ammonium vanadate [NH_4VO_3] in a Pt crucible, reacting the residue with hot nitric acid [HNO_3], and pouring the mixture into water.¹⁵⁰ The sol evolves toward a $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel, a composite material consisting of solvent H_2O molecules trapped inside a V_2O_5 oxide network.¹⁵¹ The gel is then dried to remove the remaining solvent. The results of similar experiments, but using hydrochloric acid [HCl], were published in 1904.¹⁵² V_2O_5 sols have also been obtained via the thermal-hydrolysis of VOCl_3 aqueous solutions.¹⁵³ Müller produced vanadium pentoxide gels simply by pouring the molten oxide, heated to $\sim 800^\circ\text{C}$, into water.¹⁵⁴ “Modern” processes, typically involving hydrolysis and condensation of metal alkoxides, such as $\text{VO}(\text{OR})_3$ ($\text{R} = \text{butyl} [\text{C}_4\text{H}_9]$ or $t\text{-amyl} [\text{C}_5\text{H}_{11}]$ groups), were reported as early as 1913.¹⁵⁵ Osterman¹⁵⁶ demonstrated in 1922 that vanadium pentoxide gels can be formed directly from the oxide by reacting crystalline V_2O_5 with hydrogen peroxide [H_2O_2].

Between the late 1800s and the 1920s, gels were also of considerable interest to chemists stimulated by a periodic banding phenomenon, Liesegang rings,^{157,158} due to precipitation from complex gels. Many noted chemists, including Wilhelm Ostwald¹⁵⁹ (1853–1932, German, 1909 Nobel Laureate in Chemistry for catalysis and chemical equilibria) and Lord Rayleigh (John William Strutt,¹⁶⁰ 1842–1919, English, 1904 Nobel Laureate in Physics for the discovery of argon, were involved. Ostwald discovered the process now termed Ostwald ripening in which large particles in liquid sols grow at the expense of small neighboring particles due to differences in solubility.¹⁶¹ It is now understood that Ostwald ripening, due to curvature-driven diffusion, plays an important role in determining island (and subsequent grain) size distributions during the early stages of film growth on solid substrates from both vapor^{162–165} and liquid phases^{166,167}

B. Film growth from the vapor phase

1. Sputter deposition

In an 1852 *Philosophical Transactions* paper, William Robert Grove (1811–1896), a Welsh lawyer (later, judge) and physicist described the earliest recorded description of sputter deposition and ion etching experiments.¹⁶⁸ A sketch of his

equipment is shown in Figure 29. Vacuum was achieved with a mechanical piston pump, similar to that of von Guericke as described in Sec. III A, with power supplied by Grove's version of a trough-style dc voltaic pile (similar to Figure 19) with a step-up transformer. The electrodes consisted of a copper plate, with an electroplated and polished silver surface, and a rod, which passed through a leather stopper in the top of the glass vacuum chamber, with a steel needle attached to its end. Based upon a passing comment in Grove's later papers, the small vessel attached to the rod electrode apparently contains "potassa fusa" (an early name for potassium hydroxide [KOH], a caustic deliquescent desiccant which can capture large quantities of water). The gas used to sustain the discharge was stored in a bladder.

The experiments were carried out at rather high pressures, ranging from ~ 100 to 500 mTorr, with the steel needle quite close to the silver plate (generally a separation of 0.25 cm, "but this may be considerably varied"). When using a mixture of hydrogen and air with the silver plate positive and the steel needle serving as the cathode, Grove observed thin film deposition [the layer was primarily iron oxide] on the silver substrate. The color of the oxide film "presented in succession yellow, orange, and blue tints" with increasing thickness (longer deposition time). Grove was reporting interference effects (as he himself noted later in the paper) which for a given substrate/film combination can be calibrated to provide film thickness vs. color as is commonly done today for SiO_2 and Si_3N_4 dielectric layers on Si(001) wafers. When Grove switched polarity and made the silver plate the cathode (negative), the iron oxide film was removed. In reality, there must have been a thin silver oxide layer remaining due to the competition between the steady-state rates of silver oxidation from the discharge and sputter etching. However, this layer, a few tens of \AA in thickness,¹⁶⁹ would have been too thin for Grove to observe. As Grove continued the experiment, a dark polished region

"occasioned by molecular disintegration" remained. Thus, Grove had not only removed the original oxide film, but had sputter etched into the silver substrate. The word "sputter" did not yet exist (as discussed at the end of this subsection), and Grove described the process throughout the paper as "disintegration."

Grove repeated the above experiment by sputtering the steel target in an "air vacuum" to produce a more fully oxidized film on the silver plate, then switched gases and electrode polarity to sputter "clean" the silver plate in a nitrogen discharge. In the same paper, Grove reported several more experiments in which he substituted different metals for the substrate plate as well as for the target needle, and changed discharge gases. The results were similar, but he describes observed differences depending upon the mass and ionization potential of the gas and the oxidation tendency of the metals. Interestingly, Grove realized that oxygen can form negative ions, and thus be attracted to the substrate (anode). The significance of this fact, that oxygen has a high electron attachment probability, was not fully appreciated until relatively recently. Researchers investigating the growth of high-temperature oxide superconductors and transparent conducting oxides,¹⁶⁹ which are typically deposited by magnetron sputtering, were confronted with the deleterious effects of O^- and O_2^- . The negative ions, accelerated by the same potential used to produce sputtering by positive ions incident at the target, bombard the growing film with energies that can be sufficiently high to produce residual defects and material loss by resputtering.¹⁶⁹⁻¹⁷¹

Practical applications for sputter-deposited single and multi-layer metal films used as mirrors and optical coatings on telescope lenses and eyepieces were discussed in papers published in 1877 by A. W. Wright, Yale University.^{172,173} He reported the growth of adherent noble-metal films sputter-deposited from wire targets onto glass microscope slides. Unfortunately, the films had large lateral thickness variations. However, an ingenious solution was presented in Wright's next paper. He designed a deposition system, evacuated with a Sprengel mercury pump (see Sec. III E), in which the tip of a wire target, whose length is encased in a glass tube, was mounted on a pendulum allowing movement in two dimensions such that films of uniform thickness could be "painted" onto the substrate. In Wright's words: "The perfect control of the process obtained by the use of the movable electrode will even make it possible to apply the method of local correction for the improvement of a defective figure, or to parabolize a spherical mirror by depositing the metal in a layer increasing in thickness toward the center."

Wright characterized the sputtering process spectroscopically using optical emission from ejected target atoms which are excited in the discharge. As-deposited platinum films, some with thicknesses $< 350 \text{\AA}$ (estimated using a combination of weight change, to within $10 \mu\text{g}$, for thicker films, deposition rate calibrations, and optical interference rings for thinner layers) were analyzed using optical transmission as a function of wavelength. Sputter-deposited mirror-like films were found to be more adherent than solution-grown layers and less sensitive to local delamination caused by water penetration to the film/glass interface.

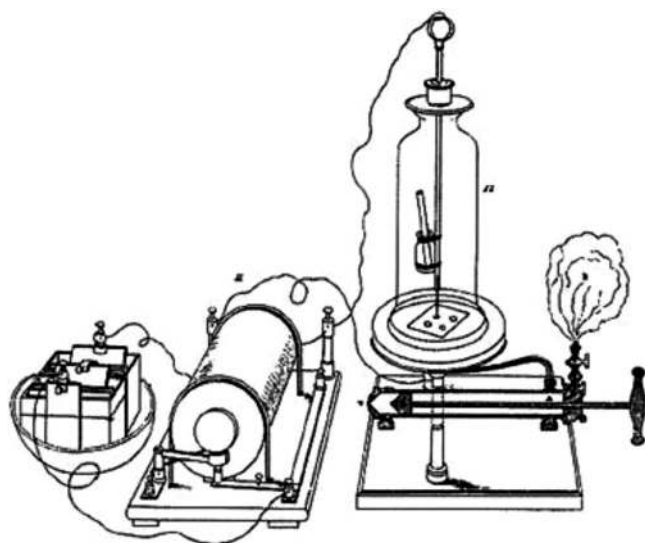


FIG. 29. The system used by William Grove to investigate target "disintegration" (sputtering) in a gas discharge. Adapted from Ref. 168. See text for details.

By the late 1800s, sputter-deposition was routinely used in manufacturing commercial mirrors.

Wright describes his films as "...surfaces of exquisite perfection and the most brilliant polish. They can only be compared to the surface of clean liquid mercury, far surpassing in luster anything that can be obtained by the ordinary methods of polishing." Wright tuned the reflectivity of his mirrors to obtain brilliant "white light" by depositing multi-layer films with predetermined layer thicknesses.

In 1891, William Crookes published a paper on sputtering in which he reported deposition rates and sputtering yields for 23 different metals.¹⁷⁴ Crookes, a British chemist, is best known for the invention of the Crooke's glow-discharge tube¹⁷⁵ which, in turn, was instrumental in the discoveries of x-rays¹⁷⁶ (Wilhelm Röntgen, 1896, Nobel Prize in Physics, 1901), electrons¹⁷⁷ (Joseph John [J.J.] Thomson, 1897, Nobel Prize in Physics, 1906), and, with thermionic emission, vacuum tube electronics. For Crookes' sputter-yield experiments, he designed a multi-target sputtering system with indexed motorized external electrical contacts as illustrated in Figure 30. Each experiment was carried out using four wire targets, 0.8 mm in diameter by 20 mm in length, in which one of the four was always a gold reference electrode. Power was alternately applied to each target in succession, using a revolving commutator, for the same length of time (typically 6 s) over periods of several hours. By this means, variations in current and sputtering pressure were accounted for to provide a set of relative metal sputtering rates referenced to Au. Since Crookes used uncooled

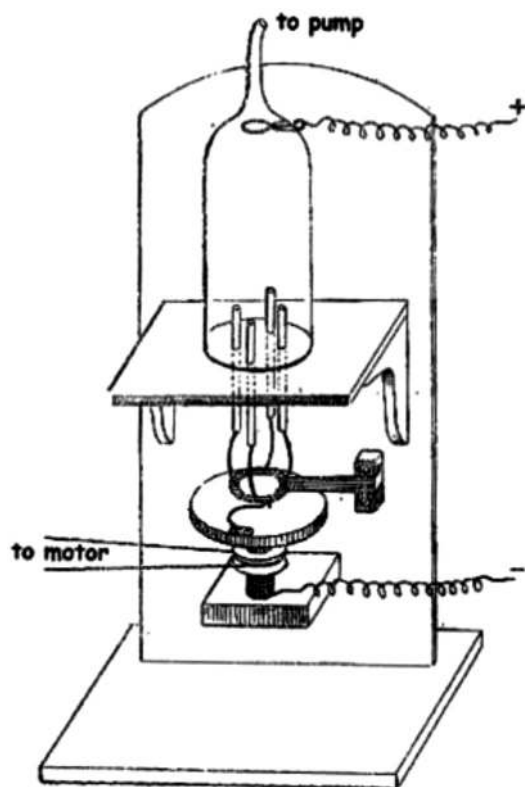


FIG. 30. The four-target sputtering system used by Crookes to measure the sputtering rates of different metals. The targets were 0.8-mm-diameter metal wires. Adapted from Ref. 174.

targets, low melting point metals such as tin, cadmium, and lead quickly melted. For these materials, he devised a holder for sputtering liquid metals.

A very early forerunner of "modern" Cu contact technology in microelectronic device fabrication is described in the 1892 U.S. patent issued to Thomas Edison¹⁷⁸ ("Process of Duplicating Phonograms") for vacuum-arc deposition of metal films on wax phonograph masters as a "seed" coat for electroplated overlayers. In 1900, he filed a second patent on the process, in this case, using dc sputter deposition, claiming that the arc process was too slow and tended to produce films with non-uniform thickness distributions.¹⁷⁹

Grove's and Crookes' research on sputtering attracted the attention of scientists worldwide. A review paper, entitled "Cathode Sputtering, a Commercial Application," published in 1932 by Fruth,¹⁸⁰ of Western Electric Company (Chicago), lists 113 references published in the field between the time of Grove's 1852 pioneering article and 1930. He also describes commercial equipment (Figure 31(a)) and procedures for sputter-depositing gold electrodes, from six gold cathodes, onto multiple radio-broadcasting microphone diaphragms. A photograph of the deposition chamber, which contains a rotating McLeod gauge and a "bleeder" valve in order to maintain constant pressure, with diaphragms ready to be coated is shown in Figure 31(b). Fruth describes the system operation as follows.

"In order to maintain a constant residual gas pressure, the pump is operated continuously and air is allowed to leak in slowly through the bleeder valve which is located near the pump. This practice was found necessary in order to overcome variations in pressure due to the early evolution of gases and the later cleanup usually accompanying electrical discharges *in vacuo*. The valve is of rugged construction as shown in the Figure [Figure 31(a)] and consists of a standard No. 0 taper pin about 2 1/2 in. [6.35 cm] long, very closely lapped into a bronze bushing. A pressure of 0.100 ± 0.005 mm [100 mTorr] is readily maintained by this method. After a new charge has been placed in the bell jar, the bleeder valve is temporarily cut off by closing a stopcock so that the required vacuum can be more quickly obtained. By this means, sputtering can be started in about 4 min after the bell jar has been placed in position."

Fruth demonstrated that dc sputter-deposited gold films, $<1 \mu\text{m}$ thick, offer substantial lifetime advantages over previous electroplated films. The electroplated layers developed "blisters," peeling, and pinholes after three months of continuous use, while the sputter-deposited films exhibited no sign of wear or degradation.

In 1926, Eric Blechschmidt¹⁸¹ carried out exhaustive studies of the sputtering yields of 19 metals by hydrogen (H_2^+), 13 metals by neon (Ne^+), and 15 metals by argon (Ar^+) ion bombardment. Unfortunately, the yield measurements of both Crookes and Blechschmidt suffer from severe target contamination due to poor vacuum. In fact, Crookes noted that aluminum and magnesium targets were "practically non-volatile."¹⁷⁴

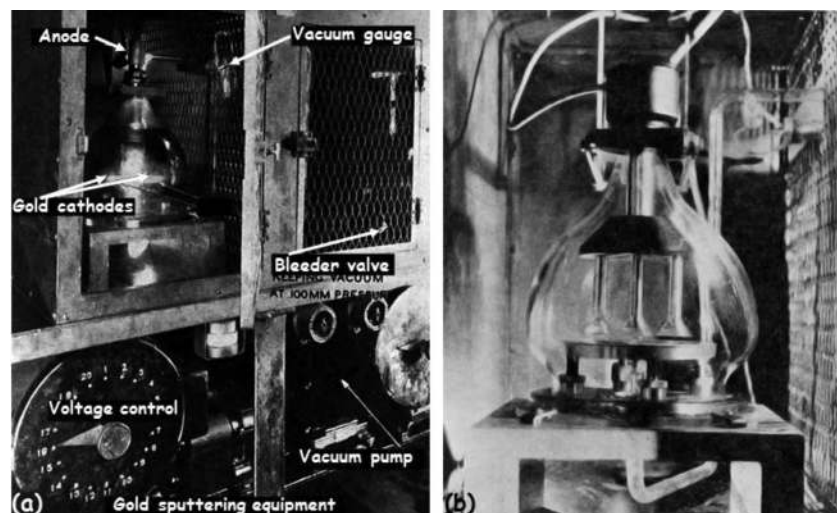


FIG. 31. (a) A commercial sputter-deposition unit, with six gold targets, for depositing metal electrodes on microphone diaphragms. (b) A closer view of the deposition chamber, showing the diaphragms. Adapted from Ref. 180; the labels were added by the present author.

Sputter-yield measurements providing results close to modern values were published by A. Güntherschulze and K. Meyer in 1931, using their newly developed high-vacuum triode glow-discharge sputtering system.^{182,183} They established a discharge of several amperes between a thermionic oxide cathode surrounded by an anode cylinder; the plasma was sufficiently dense to allow operation at pressures between 1 and 10 mTorr. Thus, the mean free path of ions and sputtered atoms was of the order of the discharge tube dimensions (ballistic transport). The target was immersed in the plasma as a third independent electrode. Güntherschulze and Meyer sputter etched the target before initiating sputtering-rate measurements and carried out separate experiments to determine the secondary-electron current and thus obtain the actual ion current at the target for accurate yield calculations. They reported a Cu sputter yield of 3.2 atoms/ion with 1 keV Ar⁺ ions, a value similar to recent results.¹⁸⁴

The first recorded description of an ion-beam sputtering system was by R. Seeliger and K. Sommermeyer in 1935.¹⁸⁵ They drilled a 2-mm-diameter hole in the cathode of their discharge tube to “collimate” positive Ar⁺ ions [actually a divergent beam] to strike solid silver or liquid gallium targets at energies of 5–10 keV and observed that sputter emission can be approximated by a cosine distribution.

In 1940, Frans Michel Penning and J. H. A. Moubis¹⁸⁶ achieved results similar to Güntherschulze and Meyer. They also operated at reduced pressures, but, in addition, introduced an axial magnetic field between the target and anode rings in order to enhance the ion current by increasing the lifetime of electrons in the discharge. They showed that with the correct magnetic field configuration, the plasma is confined near the target surface yielding increased ionization and resulting in a narrow, essentially collisionless, target sheath. They report target current densities of 20 mA/cm² at ion energies of 500–1500 eV with a background pressure of 10⁻⁵ Torr. The original co-axial cylindrical Penning discharge¹⁸⁷ is a pioneering version of magnetically enhanced dc sputtering which eventually led to the invention of the modern magnetron by John Thornton in the early 1970s.¹⁸⁸

Crookes, in 1891, compared the sputtering process to evaporation and described differences in the two processes

as arising from coupling electrical vs. thermal energy to the source material. That is, sputtering in his terminology was “electrical evaporation.” Even though contradictory evidence continued to accumulate, the concept that sputter ejection of target atoms occurs by local “hot spot” evaporation persisted well into the early 1900s. In fact, review articles published as late as the 1960s, followed Güntherschulze¹⁸⁹ in attempting to popularize the term “impact evaporation.”¹⁹⁰

In 1908, Johannes Stark (1919 Physics Nobel Laureate for his discovery of the splitting of atomic spectral lines in electric fields) argued strongly in favor of sputtering occurring by atomic impact initiating collision cascades.^{191,192} There was abundant evidence to support these claims, including the high ejection energy of sputtered atoms and the relative insensitivity of the sputtering yield to target temperature. H. Fetz added further experimental evidence in 1942 when he showed that sputtering yields increase with increasingly oblique angle of ion incidence due to more effective momentum transfer near the target surface.¹⁹³ Furthermore, Gottfried (Fred) Wehner, often referred to as the father of modern sputtering, found that atoms tend to be sputter ejected in a specular (forward) direction when subjected to oblique low-energy (<1 keV) ion bombardment.¹⁹⁴

The earliest report of radio-frequency (rf) discharges was by J. J. Thomson (1906 Nobel Laureate in Physics, as noted above), in 1891.¹⁹⁵ He employed a Sprengel-type mercury pump and applied power inductively. In 1933, D. Bannerji and Radharaman Ganguli described experiments using inductive 4 MHz rf plasmas to deposit mercury films on the glass walls of a discharge tube.¹⁹⁶ They realized that mercury atoms, from a heated source, were ionized in the discharge. In the same year, J.K. Robertson and C.W. Clapp reported the use of an inductive rf discharge for removing (ion-etching) metal layers deposited on their glass discharge tubes.¹⁹⁷ Gottfried Wehner and colleagues, in 1962, are credited with designing the first modern capacitively-coupled rf discharge for depositing dielectric thin films.¹⁹⁸

The etymology of the word sputtering is not clear. The term “spluttering,” an intensified form of the English word sputtering, meaning “to spit with explosive sounds” (a cognate for the Dutch word *sputteren*),¹⁹⁹ may have been used

as early as the late 1800s. In a 1970 book chapter, Gottfried Wehner and Gerald Anderson²⁰⁰ noted that a search of the literature revealed that Thomson still used the term sputtering in 1913 (“A well-known instance of this is the *sputtering* of the cathode in a vacuum tube;....”),²⁰¹ but Kenneth H. Kingdon and Irving Langmuir (1932 Nobel Laureate in Chemistry for his work in surface science) at the General Electric Research Laboratory dropped the “l” in favor of the word sputtering in their 1923 paper on “The Removal of Thorium from the Surface of a Thoriated Tungsten [light bulb] Filament by Positive Ion Bombardment.”²⁰² Nevertheless, in the same year, in an article on the sputtering of tungsten published in the *Philosophical Magazine* by the “Research Staff of the General Electric Company and communicated by the Laboratory Director” (Kingdon and Langmuir’s manager), the term “cathode disintegration” was used in place of sputtering. With time, however, the term sputtering prevailed and is now used universally.

a. Reactive sputter deposition. The majority of early experiments on sputter deposition of metallic thin films actually involved the growth of metal oxide layers (reactive deposition), due to poor vacuum, and most researchers realized this. Clarence Overbeck (Northwestern University)²⁰³ was the first to publish an article purposefully devoted to the study of reactive sputter deposition. He sputtered tin from a liquid target, held in a pyrex cup, using dry air, oxygen, nitrogen, and hydrogen discharges with dc potentials ranging from 1.8 to 2.6 keV. In early experiments, carried out in a fixed (non-flowing) pressure of dry air, he observed that the pressure decreased with time indicating gas incorporation in the film. Subsequent experiments were carried out at constant gas flow. Films deposited in flowing air and oxygen were oxides, with similar appearance, exhibiting interference rings which changed systematically with film thickness. Overbeck assumed that the films were stannic oxide [SnO₂].

Layers deposited in nitrogen discharges were opaque with a brown color. The films were apparently underdense since he reports that “exposing the film to air caused it to gradually lose its opacity and take on the transparent nature of films produced in air.” Overbeck demonstrated, based upon wet-chemical analyses, that the films grown in nitrogen were SnN_x. Films grown in hydrogen, which required “higher pressures,” had highly reflecting metallic mirror surfaces.

Overbeck was also the first, by several decades, to report problems with arcing during reactive sputter deposition of oxides. While he did not use modern terminology, his description of the process was correct.

“Frequently the discharge became unstable, giving rise to a sudden high-current density which pitted the cathode surface and produced a granular metallic deposit on the plate. A microscopic examination revealed that these metallic particles were of.... a rough spherical shape.... it appeared that they had been flattened on striking the deposit plate, which indicated considerable velocity of impact and heating. The metallic nature of the deposit might be explained by the fact that the particle, rapidly

deposited, was of large size and therefore its combination with gas molecules would not be favored.”

It is now well understood that arcs can occur during dc reactive sputtering of electrically conducting targets due to the formation of local insulating regions (typically oxides) on the target surface.²⁰⁴ The system rapidly switches from a high-voltage, low-current glow discharge to a low-voltage, high-current arc. All of the power is applied to the local region, which typically ranges from $\sim 10^{-2}$ to 100 μm in diameter, resulting in the current density increasing by many orders of magnitude, local heating leading to thermionic emission, and a micro-explosion. Thermal runaway causes local melting and boiling of solid targets over time scales of order ns giving rise to the ejection of macroscopic liquid droplets with very high velocities which can land on the growing film surface²⁰⁵ as Overbeck reported. Scanning electron micrographs showing the effect of an arc on a target surface (leaving an $\sim 12 \mu\text{m}$ diameter pit) and collateral effects of arcing on film growth are shown in Figure 32. There are, today, a variety of solutions available for solving, or at least minimizing, the arcing problem; they all involve fast arc detection circuitry, dumping excess power into a bus bar, and periodically (typically 50–350 kHz or 13.56 MHz) switching the power supply to neutralize accumulated positive charge as discussed in Ref. 169.

The mercury-pumped deposition system used by Overbeck,²⁰³ Figure 33, is itself of interest since it contained, in 1933, many of the features, although in a slightly different guise, found in modern ultra-high vacuum systems: vacuum gauging (a McLeod gauge, see Sec. III E), multiple chambers, liquid nitrogen (here liquid air) traps, gas scrubbers, facilities for multiple substrates, a magnetically coupled rod to transport substrates in and out of the deposition chamber, and the capability to controllably vary the target-to-substrate distance via a second magnetically coupled rod. Note that opening the system to retrieve the deposited films required breaking the end of the side tube (the reason, of course, for multiple substrates), and reforming it by glassblowing. A description of the apparatus, in Overbeck’s words, follows.

“A steady potential, variable from 1800 to 2600 V, was applied between the aluminum anode, D, and the tin cathode, F (2 cm in diameter and 2 cm long). The cathode was placed in a Pyrex cup with its surface flush

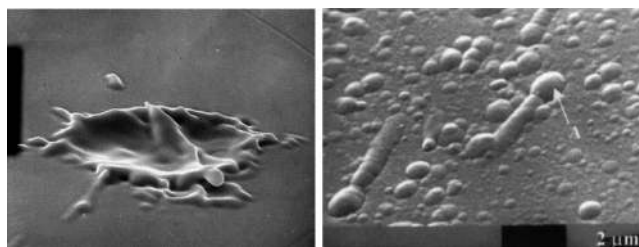


FIG. 32. Left figure is a scanning electron micrograph of an $\sim 12\text{-}\mu\text{m}$ -diameter pit formed at a metal target surface due to arcing (image courtesy of Dr. Andre Anders, Lawrence Berkeley National Laboratory). The right figure shows embedded metal droplets in an underdense Al₂O_x film deposited by reactive sputter deposition from an Al target in a mixed Ar/O₂ atmosphere. Adapted from Ref. 206.

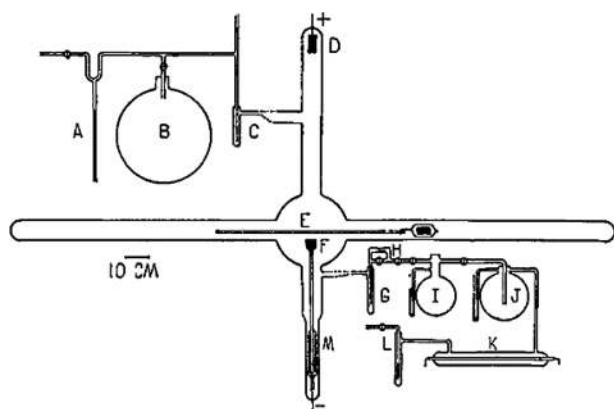


FIG. 33. Pyrex vacuum system used by Overbeck (adapted from Ref. 203) to investigate sputter-deposition of Sn in dry air, O₂, N₂, and H₂ environments. See text for detailed description.

with the top of the cup. The deposit formed on a Pyrex plate, E (3 cm wide and 45 cm long). The distance between cathode and plate was adjustable and held by an electromagnet acting on a glass-enclosed piece of soft iron, M. The deposit plate could be drawn back and forth in the side tubes by a second electromagnet. This permitted making from six to ten deposits before blowing out the end of the side tube to remove the deposit plate. The sputtering chamber was separated from the remainder of the system by liquid air traps, C and G. A McLeod gauge was attached above C. A 12 liter bottle, B, was placed in the system to stabilize the gas pressure. This added volume reduced the pressure variation caused by the vigorous “cleanup” action which was especially large at the beginning of a run. A high-vac pump was attached beyond the mercury cut-off, A. The lower right-hand corner (of the figure) shows the gas purifying chambers. Water vapor, carbon dioxide, and oxygen were removed from the incoming gas by phosphorus pentoxide in J, sodium hydroxide in L, and hot copper gauze at K. The gas was finally collected for use in flask, I, from which it could be admitted into the sputtering system by either of two methods: (1) A capillary opening at H permitted a constant flow of fresh gas through the system. With the pump in operation, proper adjustment of the pressure in I gave any desired pressure in the system. (2) Known quantities of gas could be admitted periodically by means of the stopcocks at H.”

As described in the book *Sputter Deposition* by W. D. Westwood,²⁰⁷ an early application of reactive sputtering in the 1950s derived from his research on the deposition of N-doped Ta films, by dc sputtering from a Ta target in mixed Ar/N₂ discharges, for use as tuned trimming resistors in hybrid circuits. Increasing the N₂ flow rate resulted in the formation of TaN_x films with the appropriate temperature coefficient of resistivity (TCR) for use in tuned circuits in touch-tone telephones. Figure 34 is a plot of TaN_x resistivity and TCR vs. N₂ flow rate.

b. Web coating by sputter deposition. The 1930s saw the advent of roll-to-roll web coating in which soft materials

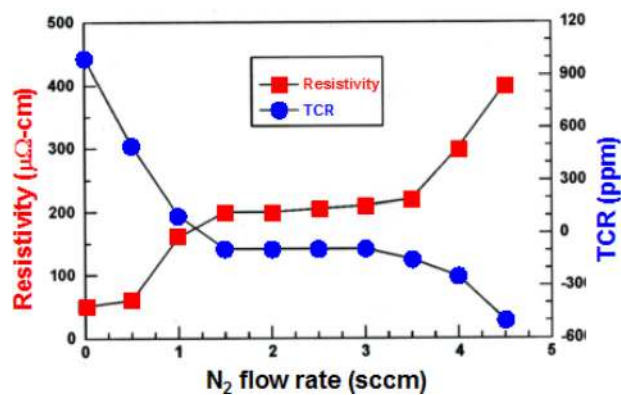


FIG. 34. Variation, as a function of the N₂ flow rate, of the resistivity and the temperature coefficient of resistivity (TCR) of TaN_x films grown by dc sputtering Ta in mixed Ar/N₂ atmospheres. Adapted from Ref. 207.

such as textiles, plastic sheets, or paper are wound on a spool and continuously passed, via a winding system which maintains constant pressure, over the vapor source and the coated material is rewound onto a take-up spool. The evolution of this technology is described in a paper by E. D. Dietrich *et al.* (Leybold Systems, Germany) in 1997.²⁰⁸ The earliest systems employed sputter deposition, then moved to evaporation in the 1940s due to higher deposition rates, and back to sputtering in the 1980s following the invention of the magnetron.¹⁸⁸

The first commercial web-coating application was in 1934; systems were installed in London and Fürth (Bavaria, Germany) to sputter deposit gold on glassine (smooth, glossy paper, with oriented fibers highly impervious to moisture) to create foil for hot stamping in specialty printing processes for producing shiny decorative designs on textiles, wood, hard plastics, leather, and other materials. In initial operations, 400 m² of glassine, on a 1-m-wide roll, was coated in 23 h. This was equal to a week’s production of gold leaf by 30 highly skilled gold-beating craftsmen. Moreover, the product had a much more uniform thickness distribution. In 1936, a web coater was installed in Boston for depositing silver on cellophane.

An early web coater (mid 1930s), designed by Bosch (Germany) for metallizing paper to produce capacitors is shown in Figure 35. By the time production was initiated, the system incorporated thermal evaporation (see Sec. IV B 4 b) rather than sputter deposition.

2. Arc deposition

Joseph Priestley (1733–1804),^{209,210} a tutor at Warrington Academy in the UK, minister, and vocal dissenter of the Church of England, demonstrated the growth of metal oxide films in the mid-1760s by cathodic-arc deposition in air. The experiments were powered by high voltage, relatively low current, Leiden-jar type batteries (see Sec. III B). Priestley published a definitive *History and Present State of Electricity* in 1767 (Ref. 66) and in a later volume added his own results on arcs at metal surfaces.²¹¹ A fascinating account of the origin of cathodic-arc deposition, with a

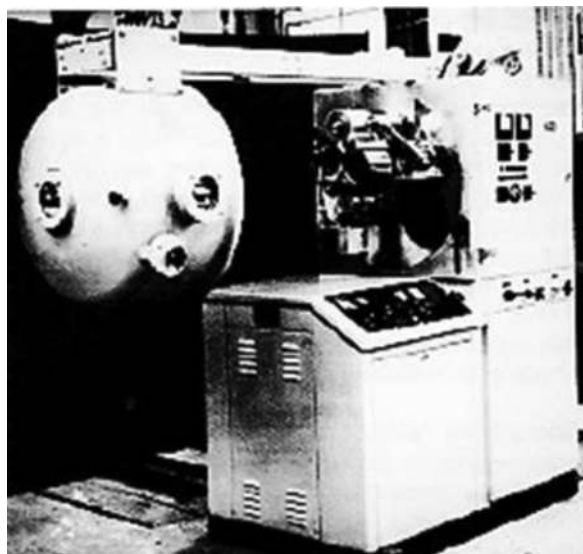


FIG. 35. Continuous roll-to roll web coater designed by Bosch (Germany) in the mid-1930s to metallize paper for the production of capacitors. Adapted from Ref. 208.

detailed discussion of Priestley's contributions, is provided by Andre Anders.²¹²

In 1857, five years after Grove published the first article on sputtering, Michael Faraday (1791–1867) reported vacuum-arc deposition of films on glass substrates in order to investigate the optical properties of metals.¹⁴⁰ Faraday, an English scientist famous for his work in electromagnetics and electrochemistry, had no formal education past grade school. However, he is considered by science historians to be one of the most influential scientists, and the best experimentalist, in history.^{213,214} Faraday used the evocative term “deflagration” to describe the arc deposition process. The following is a quote from Ref. 140.

“When gold is deflagrated by the voltaic battery near glass (I have employed sovereigns laid on glass for the terminals), a deposit of metallic gold in fine particles is produced. The densest parts have a slate-violet colour passing into violet and ruby-violet in the outer thinner portions; a ruby tint is presented occasionally where the heat of the discharge has acted on the deposit..... I prepared an apparatus by which many of the common metals could be deflagrated in hydrogen by the Leyden battery, and being caught upon glass plates could be examined as to reflexion, transmission, colour, &c. whilst in the hydrogen and in the metallic, yet divided state. The following are briefly the results; which should be considered in connexion with those obtained by employing polarized light. *Copper*: a fine deposit presenting by reflexion a purplish red metallic lustre, and by transmission a green color, dark in the thicker parts, but always green;.... *Tin* gave a beautiful bright white reflexion, and by transmission various shades of light and dark brown;.... *Iron* presented a fine steel grey, or slate metallic reflexion and a dark brown transmission.... *Lead*: a bright white reflexion, the transmission a dark smoky brown;.... *Zinc*: the reflexion bright

white and metallic; the transmission a dark smoky colour with portions of blue-grey, brown-grey, and pale brown;.... *Palladium*: the reflexion fine metallic and dark grey; the transmitted light, where most abundant, sepia-brown;.... *Platinum*: the reflexion white, bright, and metallic; the transmission brown or warm grey with no other colours;.... *Aluminium*: the reflexion metallic and white, very beautiful; the transmitted light was dark brown, bluish brown, and occasionally in the thinner parts orange;....”

3. Chemical vapor deposition (CVD) and plasma-enhanced CVD

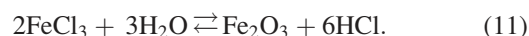
The use of a hot charcoal fire to reduce metal ores can be traced back to ~5000 BC (see Sec. II).^{7,39} The Roman philosopher Pliny the Elder discusses the process in his 37-book *Naturalis Historia*,³⁶ published ~79 AD.

In 1649, Johann Schroeder, a German pharmacist, reported a method for reducing arsenic oxide [As_2O_3] with charcoal^{215,216} through the overall reaction

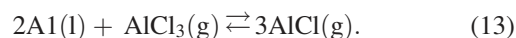


As discussed in a review article by Rolsten,²¹⁷ carbon reduction of oxides was an important method for obtaining relatively pure metals, in order to investigate their physical properties, during the 1700s and early 1800s: nickel in 1751, manganese in 1774, molybdenum in 1781, tungsten in 1783, chromium in 1798, and cadmium in 1817.

An important step toward modern CVD processes occurred in the mid-1800s as chemists investigated metal transport via heterogeneous reactions in the vapor phase. Robert Bunsen²¹⁸ (1811–1899), a German chemist at the University of Heidelberg, co-inventor of the Bunsen burner, reported the migration of ferric oxide [hematite, Fe_2O_3] in a stream of HCl, associated with the smell of “volcanic gases,” through the reversible reaction:



Halide reactions were also studied by French mineral chemists. H. Sainte-Claire Deville investigated SnO_2 , TiO_2 , and MgO transport in halides.²¹⁹ L. Troost and P. Hautefeuille reported what are now termed formation and disproportionation reactions with silicon²²⁰ in 1876 and aluminum²²¹ in 1885:



Werner Siemens (1816–1892), a German industrialist interested in electronics, published the first paper on the use of atmospheric plasmas in 1857; his objective was ozone [O_3] production.²²² Investigations in 1869 by Marcellin Berthelot (1827–1907), a famous French synthetic chemist, on the decomposition of gases such as methane [CH_4] in glow discharges²²³ led to the development of plasma-enhanced chemical vapor deposition (PE-CVD). In 1876, J.

Ogier reported PE-CVD growth of Si:H and SiN_x films from silane [SiH₄] and SiH₄ + N₂ precursors, respectively.²²⁴

W. E. Sawyer and A. Man were issued a patent in 1880 for thermal CVD of C films, using hydrocarbon precursors, onto carbon rods in order to increase their lifetime in incandescent lamps.²²⁵ They note: “Carbon [rods] of the ordinary sort, when heated by the electric current, exhibits points and lines of unequal brilliancy.” That is, the rods were both underdense and impure. Sawyer and Man developed a process in which a carbon rod was placed in a pure hydrocarbon gas or liquid and raised to “an extremely high temperature” via Joule heating. The hydrocarbon gas (presumably the temperature was sufficiently high that the rod was surrounded by hydrocarbon gas even in the liquid) decomposes in a pyrolytic reaction such that carbon “enters and fills up the pores [in the rod].... and deposits a perfectly homogeneous layer, generally of a bright gray color, upon the exterior surface.... As the carbon [rod] increases in size, more current is required to increase its temperature.” The dense carbon rod with a “pure” carbon coating is then cleaned in alcohol and placed in a lamp which is hermetically sealed.

Ludwig Mond, an English chemist, and his colleagues reported CVD of mirror-like nickel films from nickel carbonyl [Ni(CO)₄] in 1890.²²⁶ The group was apparently the first to synthesize nickel carbonyl. The process was initiated with finely divided Ni particles formed by reducing nickel oxide [NiO] in hydrogen at ~400 °C; the Ni was then slowly cooled in a flow of carbon monoxide [CO]. At a temperature of ~100 °C, Mond *et al.* obtained a gas consisting of “nickel-carbon-oxide” which they chemically decomposed into CO and Ni, measured the relative volumes, and determined the gas composition. The metal carbonyl was then used as a precursor for the CVD growth of pure Ni films at 180 °C. They also obtained Ni deposits via spark decomposition of Ni(CO)₄. Mond was issued a U.S. patent a year later for Ni CVD by Ni(CO)₄ decomposition on clean metallic or graphite-coated surfaces at temperatures ≥ 180 °C.²²⁷

In 1896, Jonas Aylesworth—a New Jersey chemist and inventor, who worked for some years with Thomas Edison, and was later inducted into the “Plastics Hall of Fame”—patented a pyrolytic CVD process for the growth of refractory metal films via hydrogen reduction of metal halides.²²⁸ The application, like that of Sawyer and Man in 1880, was aimed at the production of longer-lived filaments in incandescent lamps. However, the approach was quite different. In this case, the metal films were deposited on carbon wire filaments as shown in Figure 36. A refractory metal halide such as niobium pentachloride [NbCl₅], a yellow crystalline solid, labeled S in the figure, is placed in the bottom of a glass bulb G, which is itself partially encased in a heated chamber A, with outlet D. The chamber is equipped with a series of Bunsen burners B. Hydrogen gas flows into bulb G through tube T, and out through T¹, while the carbon filament C is heated via a current flowing through leads w and w', the latter passing through a high-temperature stopper (probably porcelain or glass, cemented in place). While the patent does not provide any estimate of the temperatures involved or discussion of the chemistry, the overall endothermic “cold wall” reaction must have been

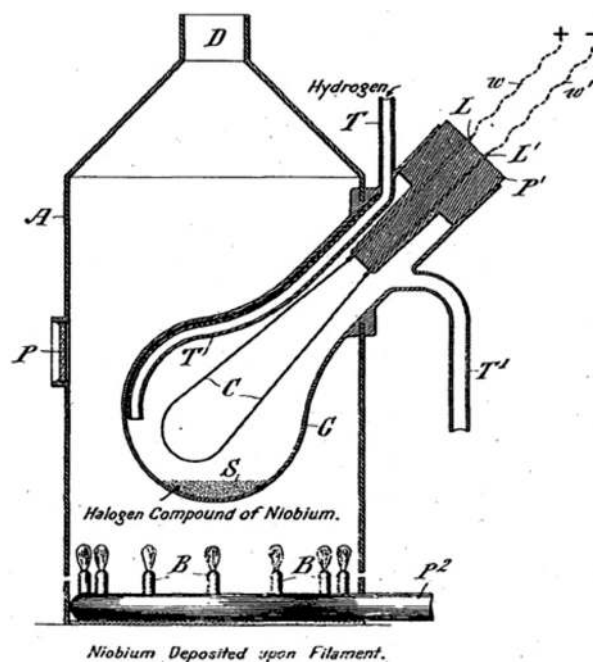
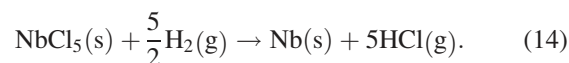


FIG. 36. Schematic diagram of the system used by Aylsworth to deposit refractory metal films on carbon lightbulb filaments by CVD from metal-halide precursors in order to increase filament lifetimes (see text for details). Adapted from Ref. 228.



Continuing the research on metal halide precursors, M. A. Hunter²²⁹ in 1910 deposited 99.9% pure bulk titanium via sodium reduction of titanium tetrachloride [TiCl₄] in a closed container. He notes in the introduction of his paper that all previous attempts to isolate pure titanium resulted in substantial concentrations of nitrides, oxides, and other impurities. His own experiments required, as he points out, “exceptional care” in purifying the reactants and maintaining the system free of air and other contaminants. He obtained approximately 70 g of pure titanium and used it to estimate the melting point of the metal as being no higher than 1800–1850 °C (it is 1660 °C) and the specific gravity as 4.5 (it is 4.54). He discusses in Ref. 229 the importance of purity in his experiments: “Among the metals which are known to us at the present day, there are few which have given rise to so great a diversity of opinion as the metal titanium. This diversity has arisen entirely from the difficulty experienced in isolating the pure metal.” (See also Ref. 230.) In 1914, D. Lely and L. Hamburger,²³¹ at Philips, Eindhoven (The Netherlands), reported obtaining pure thorium, uranium, zirconium, and titanium through the reduction of metal tetrachloride gases with sodium. Irving Langmuir,²³² while investigating the lifetime of tungsten light bulb filaments, showed that at low pressures, oxygen, and chlorine will react with tungsten at elevated temperatures to form WO₃ and WCl₆, the latter a common precursor for tungsten CVD today. He also reported deposition of tungsten films, presumably by hydrogen reduction, at cooler regions of the light bulb.

In 1911, Werner von Bolton (1868–1912), a German chemist, described CVD growth of diamond on seed crystals.

The process was based upon the decomposition of acetylene [C_2H_2] in the presence of mercury vapor from an amalgam held at $100^\circ C$ for three weeks.²³³ He claimed that the fraction of amorphous carbon was small. Otto Ruff (1871–1939), another German chemist, reported in 1917 that small diamonds did not increase in weight when heated for 14 days in C_2H_2 , coal gas, methane [CH_4], or carbon monoxide [CO] at temperatures of up to $790^\circ C$.²³⁴ He did, however, produce amorphous carbon and graphite by passing organic vapors and salts through a carbon arc. Gustav Tammann (1861–1938), a Baltic physical-chemist/metallurgist synthesized carbon, which exhibited no evidence of crystallinity, in 1921 by heating mercury vapor with carbohalide gases— CCl_4 , CBr_4 , or Cl_4 —in glass tubes at 600 – $700^\circ C$.²³⁵ He also presented an early temperature/pressure phase diagram for the carbon system. CVD of carbon-containing films by electron-beam (1 – 18×10^{-6} A, 190 – 210 V) stimulated dissociation of adsorbed adventitious hydrocarbons in a vacuum system with a base pressure of $\sim 10^{-5}$ Torr was reported in 1934.²³⁶

4. Thermal evaporation

Joseph Stefan (1835–1893), a physicist born near what is today Klagenfurt, Austria, is best known for his seminal work on thermal conductivity of gases and blackbody radiation from solids.²³⁷ However, he also carried out some of the first vapor pressure measurements during his studies of gas diffusion.^{238–240} His experimental apparatus consisted of glass tubes, open at the top, partially filled with a liquid and held at constant temperature. The tubes were both long and narrow to avoid a significant temperature decrease at the evaporating surface. A summary of key results includes the following. (a) The evaporation flux J_e from the tube decreases as the liquid level drops. Note that associated “beaming” effects (the tendency toward forward emission of molecules as the liquid level in the tube decreases), resulting in changes in lateral film thickness uniformity during molecular-beam evaporation from crucibles,²⁴¹ continue to be a problem more than 100 years later. (b) Over a relatively wide range, J_e is independent of the tube diameter. (c) J_e increases with temperature due to the corresponding increase in the liquid vapor pressure.

Heinrich Hertz (1857–1897), a German physicist, well known for his work on both electromagnetics²⁴² and contact mechanics,²⁴³ also had an important impact on the evolution of evaporation theory.^{244,245} Hertz, while working at the Berlin Physical Institute, carried out the first systematic investigation of vacuum evaporation rates using mercury as

the evaporant.²⁴⁴ He determined evaporation losses from the liquid mercury source material while simultaneously measuring the hydrostatic pressure exerted on the evaporating surface. The relatively high thermal conductivity of mercury insured that the evaporation rate R_e was not limited by insufficient heat supply to the surface.

From the experimental results, Hertz drew two important fundamental conclusions. (1) The evaporation rate cannot exceed a certain maximum value $R_{e,max}$ at a given temperature even if the heat supply is unlimited. (2) The maximum evaporation rate corresponds to the situation in which the rate of atoms leaving the evaporant surface is equal to the flux J_e required to exert the equilibrium vapor pressure P_e on the same surface. The latter condition requires essentially perfect vacuum such that there is no hydrostatic pressure P_i acting on the surface, i.e., no evaporated atoms return to the surface. In this case, $R_{e,max} \equiv J_e$, as illustrated in Figure 37(a), and J_e is directly related to P_e via standard gas kinetics²⁴⁶ such that

$$R_{e,max} = J_e = 3.513 \times 10^{22} P_e / (m T_e)^{1/2}, \quad (15)$$

in which P_e is in units of Torr, m is the mass of the evaporating atom in amu, and T_e is in K.

The initial evaporation rates measured by Hertz were far less than the maximum rates; in fact, R_e was only $\sim 0.1 R_{e,max}$ and he immediately realized that the hydrostatic pressure P_i has to be accounted for. At equilibrium in a closed system, the vaporization flux J_e must be equal to the incident flux J_i by detailed balance (microscopic reversibility), and $R_e = 0$. However, in an open system such as Hertz was using (and in a deposition experiment), some of the vapor is continuously lost to the pumps and to condensation on cold surfaces (the substrate and system walls). Thus, $J_e > J_i$, and Hertz deduced that $R_e \propto (P_e - P_i)$ as illustrated in Figure 37(b).²⁴⁴ Thus, the Hertz evaporation equation can be expressed as

$$R_e = (J_e - J_i) = 3.513 \times 10^{22} (P_e - P_i) / (m T)^{1/2}. \quad (16)$$

However, measured R_e values were still low and the issue was not resolved until 1915, 33 years later, by Martin Knudsen²⁴⁷ as discussed below.

In 1884, Thomas Edison was issued a U.S. patent for vacuum evaporation (and arc deposition) of both conducting and non-conducting materials which were previously “coated” (presumably by electroplating) onto a carbon rod. The rod was heated by dc current.²⁴⁸ He noted that “The uses of this invention are almost infinite,” although there is

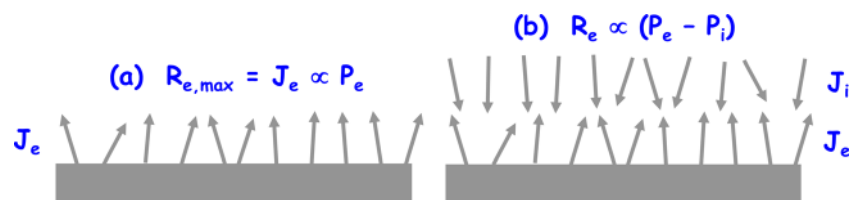


FIG. 37. (a) Schematic illustration of evaporation, at temperature T_e , into perfect vacuum with no flux returning to the liquid surface. The maximum evaporation rate $R_{e,max}$ is equal to J_e , the flux required to exert the equilibrium vapor pressure at T_e . (b) As in (a), but accounting for a hydrostatic pressure P_i giving rise to a flux J_i incident at the evaporant surface.

no evidence that he ever employed the idea in his subsequent work. He also discussed various methods of forming metal foil, “especially gold, silver, and platinum foil,” by using a substrate of glass which is pre-coated with a film that is soluble in a liquid, such as alcohol or water, then overcoating it with evaporated metal. The bilayer is later stripped off as a “homogeneous sheet” and the underlayer dissolved. This is an early example of using what is now termed a sacrificial thin-film interfacial release layer for producing free-standing foil.^{249–251}

R. Nahrwold, in 1887, reported the vacuum deposition of platinum films by direct vaporization from solid platinum, without melting the evaporant, using Joule heating.²⁵² A general guideline for obtaining a reasonable thin-film deposition rate is that the equilibrium vapor pressure P_e should be $>10^{-2}$ Torr, which corresponds to a mass deposition rate $>10^{-4}$ gm cm $^{-2}$ s $^{-1}$ for many elements.²⁵³ Today, it is well known that several solids (for example: arsenic carbon, chromium, iron, magnesium, palladium, silicon, silicon monoxide [SiO], vanadium, zinc, and zinc sulphide [ZnS])²⁵⁴ reach sufficiently high vapor pressures prior to melting that vaporization and film deposition can be achieved from the solid phase; a process termed sublimation. Experiments, similar to those of Nahrwold, were carried out by A. Kundt a year later in order to measure refractive indices of metal films.²⁵⁵

In 1907, Frederick Soddy (1877–1956, English, 1921 Nobel Laureate in Chemistry for his seminal investigations in nuclear and isotope chemistry) reported that while vaporizing calcium in vacuum, “If air is introduced into the apparatus, all but argon is rapidly adsorbed.”²⁵⁶ He had invented the first continuous getter pump for decreasing background reactive partial pressures in a vacuum deposition chamber! He goes on to say that “In a similar way it was shown that carbon monoxide, carbon dioxide, water vapour, hydrogen, acetylene, sulfur dioxide, ammonia and the oxides of nitrogen.... are all as readily and completely adsorbed as in the case of the oxygen and nitrogen of the air.” Modern getter pumps (today called capture pumps) typically use reactive metals such as zirconium- or titanium-based alloys, either as small particles with large surface-to-volume ratios, or continuously deposited, via sublimation or sputtering.²⁵⁷

Martin Knudsen (1871–1949), a Danish physicist at the Technical University of Denmark and famous for his work on low pressure gaseous molecular flow (Knudsen flow, the Knudsen number)²⁵⁸ and the development of the Knudsen evaporation cell for accurate vapor pressure measurements,²⁵⁹ realized that the Hertz evaporation story was not complete. He argued that a fraction of the particles impinging on the evaporant surface can be reflected (due, for example, to surface contamination—primarily surface oxides for

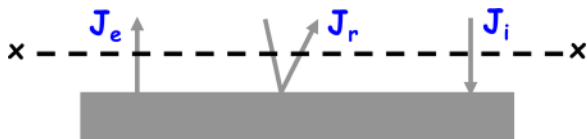


FIG. 38. Illustration of evaporation in which J_e is the vaporized flux, J_i is the hydrostatic flux incident at the evaporant surface, and J_r is the flux of reflected incident species.

the mercury charges used in Hertz’s experiments). He therefore introduced an “evaporation coefficient” α_v (sometimes called the quality factor) which accounts for the fact that a fraction $(1 - \alpha_v)$ of vapor molecules contribute to J_i , but not to the net flux $(J_e - J_i)$ from the condensed to the vapor phase.²⁴⁷ This further decreases R_e .

Detailed balance must still apply; thus, the incident and effusing fluxes crossing a line x-x a few Å above the evaporant surface, as shown schematically in Figure 38, must be equal. Therefore,

$$R_e = (J_e + J_r - J_i) = \alpha_v (J_e - J_i), \quad (17)$$

$$R_e = 3.513 \times 10^{22} \alpha_v (P_e - P_i) / (mT)^{1/2},$$

where J_r is the reflected flux. The above expression is commonly labeled the Hertz-Knudsen equation, for which the reflected flux J_r is given by the expression

$$J_r = (J_e - J_i)(\alpha_v - 1). \quad (18)$$

For an evaporation coefficient (quality factor) $\alpha_v = 1$, $J_r = 0$. At the other extreme, if $\alpha_v = 0$, then $J_r = -(J_e - J_i)$ and the net evaporation rate $R_e = 0$. Note that if $\alpha_v = 0$ and $J_e = 0$, all particles are reflected and $J_r \equiv J_i$.

Knudsen showed that the evaporation coefficient α_v is strongly dependent on evaporant purity. In his initial experiments, for which mercury surface contamination was visible to the eye as discoloration, he obtained α_v values as low as 5×10^{-4} . In later experiments, with distilled pure mercury droplets, he obtained evaporation rates essentially equal to theoretical maximum values.²⁴⁷

To accurately determine equilibrium vapor pressures P_e from direct evaporation measurements (i.e., $R_e \propto J_e \propto P_e$ with $\alpha_v = 1$), Knudsen developed what is now called the Knudsen cell as illustrated schematically in Figure 39. The crucibles used today in standard III–V and II–VI molecular beam evaporation (MBE) systems²⁴¹ are often called Knudsen cells (or K-cells), but, for practical reasons, they are quite different with much larger orifices (in order to achieve reasonable deposition rates and lateral film thickness uniformities) and are better referred to as effusion cells.

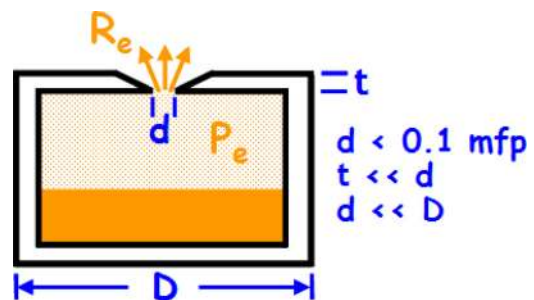


FIG. 39. Schematic illustration of a Knudsen cell, maintained at constant temperature T_e , in which the evaporated flux effuses from an orifice of diameter d , small compared to the evaporant surface area, such that the pressure inside the cell remains constant at the equilibrium evaporant vapor pressure $P_e(T_e)$. The orifice diameter d must also be much less than the evaporant mean free path, but much larger than the wall thickness t at the edge of the orifice. See text for details.

Knudsen's strategy was to allow evaporation to occur as effusion from an isothermal enclosure, with a very small orifice, in a clean environment under high vacuum. The evaporating surface within the enclosure is large compared to the orifice and maintains the pressure inside at $P_e(T_e)$. The orifice diameter is much less than 0.1 of the gas mean free path at P_e and the wall thickness at the orifice is made vanishingly thin to inhibit scattering or adsorption/desorption at the orifice wall. Under these conditions, the orifice constitutes an evaporating surface with an evaporant pressure P_e and $P_r \sim 0$. Thus, $\alpha_v = 1$ and $R_e \propto (P_e - P_i)$. If the experiment is in ultra-high vacuum and the Knudsen cell encapsulated in a liquid-nitrogen cooled shroud, $R_e \propto P_e$. In addition to measuring vapor pressures, Knudsen deposited films by evaporation.²⁶⁰

It was shown by Irving Langmuir that the Hertz-Knudsen equation also applies to vaporization from solid surfaces (sublimation, as defined above). He investigated the evaporation of tungsten from filaments in evacuated glass bulbs.²⁶¹ By measuring the filament weight loss as a function of temperature for a given period, establishing that the system pressure was low enough to ignore J_i , and showing that $J_r = 0$,²⁶² he determined the vapor pressure of tungsten over the temperature range from 2440 to 2930 K (2167 to 2657 °C). He then fit the results to the Clausius-Claperyon equation to obtain the enthalpy of vaporization over this temperature range, 217.8 kcal/mole (9.45 eV/atom), which is in reasonably good agreement with modern values. In the same paper, Langmuir reports depositing tungsten films on the glass enclosure; in Ref. 263, he provides the temperature-dependent vapor pressures of platinum and molybdenum.

R. von Pohl and P. Pringsheim deposited several metals, including aluminum and silver, by evaporation from a magnesium oxide [MgO] crucible, to produce mirrors.²⁶⁴ In 1928, R. Ritzl produced half-silvered interferometer mirrors by evaporation from a tungsten coil.²⁶⁵ A simple, but effective, method for producing mirrors was reported in 1933 by John Strong (California Institute of Technology) who evaporated aluminum from helical-shaped large-diameter tungsten filaments.²⁶⁶ He showed that tungsten has a relatively low solubility in molten aluminum (~ 3 vol. %). Chemical analysis of the resulting film revealed no detectable tungsten incorporation (detection limit ~ 0.03 wt. %).²⁶⁷ Moreover, aluminum, due to its strong oxide bond, is much more adherent than silver to glass substrates. A typical coiled tungsten filament used in Strong's experiments, 0.8 cm in diameter with a pitch of 1.6 turns/cm, is shown in Figure 40. In the upper panel, U-shaped pieces of aluminum wire, 1 mm in diameter and ~ 1 cm in total length, are clamped to each tungsten turn. Applying current through the filament melts and flows the aluminum (middle panel) which remains in place due to surface tension. The bottom panel shows the filament after aluminum evaporation. Strong also developed a technique for evaporating platinum by first electrodepositing a thick platinum coating onto a tungsten filament.²⁶⁸ This technique is still utilized today.

In the early 1930s, there was considerable interest in thin film radiation detectors such as radiometers, thermopiles, and surface bolometers. For these applications, it was

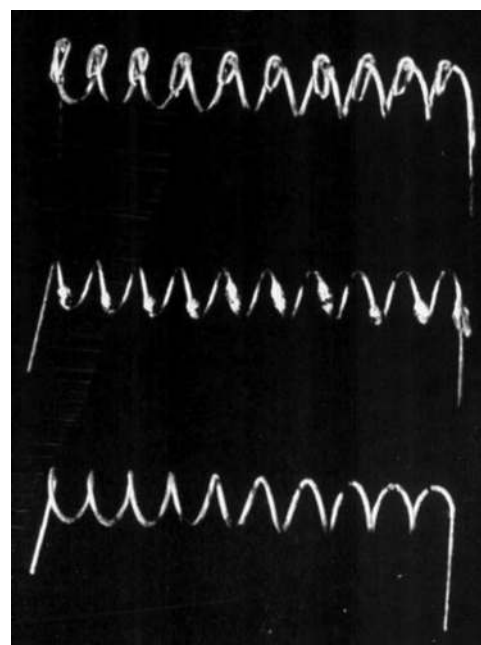


FIG. 40. Photographs of 0.8-cm-diameter tungsten filaments used to evaporate aluminum. In the upper panel, U-shaped pieces of aluminum wire, 1 mm in diameter and ~ 1 cm in total length, are clamped to each tungsten turn. The middle photograph shows a filament after heating to melt the aluminum pieces and form a continuous coating on the wire, while the bottom panel shows a tungsten filament following aluminum evaporation. Adapted from Ref. 267.

necessary to develop a film that functions as a black body and is opaque ("black") to visible light. A. Hermann Pfund of Johns Hopkins University accomplished this by evaporating metal layers,^{269,270} including bismuth, selenium, tellurium, and zinc, as well as salts²⁷⁰ such as sodium chloride [NaCl] and thallium chloride [TlCl] at high pressures, up to 3–5 Torr, to produce films consisting of large coarse particles which formed primarily due to gas-phase reactions. The researchers had no access to techniques to measure particle size or size distributions, but optical measurements showed that the films were indeed "intensely black" in the visible and highly transparent in the infrared. Thus, average particle sizes must have been of the order of visible light, in the sub-micron range, in order to trap incident radiation.

Figure 41 is an illustration of Pfund's vacuum system, with a 0.18-mm-diameter tungsten spiral filament (labeled F), used in these experiments. The glass bell jar A is sitting on a polished metal plate B and sealed with a "solid solution of vaseline and paraffin melted into the trough C to form a vacuum-tight seal." The filament is connected, via "small brass blocks," to electrical leads which pass through, and are cemented to, a ground glass tube.

Pfund also grew compound thin films, reporting in 1934 the deposition of zinc sulphide [ZnS] layers by thermal evaporation in order to produce low-loss beam splitters for Michelson interferometers.²⁷¹ He observed that "this material may be distilled [vaporized], with but little decomposition, from an incandescent tungsten spiral in high vacuum [$< 5 \times 10^{-4}$ Torr]." Today, it is known that zinc sulphide sublimates dissociatively,

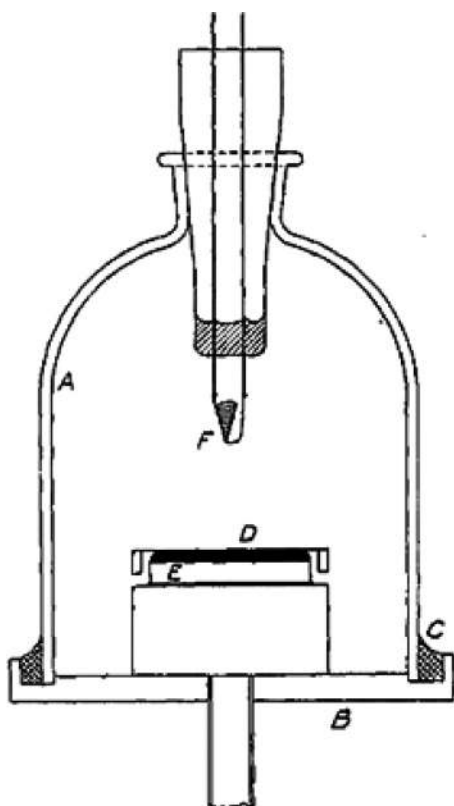
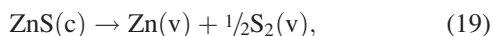
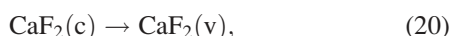


FIG. 41. Vacuum system used to evaporatively deposit “black” metal films which are opaque throughout the visible spectrum. The glass bell jar A is sealed (C) to a polished metal plate B. Small metal pieces are melted and evaporated from a tungsten filament F and a metal film deposited on substrate D. Adapted from Ref. 270.



but congruently as stoichiometric vapor.²⁵⁴ The designations *c* and *v* in Eq. (19) refer to the condensed and vapor phases. In 1936, John Strong produced antireflection coatings by evaporation, at pressures of 10^{-3} – 10^{-1} Torr, of “fluorite” [calcium fluoride, CaF_2] to form inhomogeneous films that reduced glass reflectance in the visible by 89%,²⁷² a remarkable achievement in that era. Calcium fluoride evaporates congruently and non-dissociatively



over a narrow range in temperatures.²⁵⁴

The earliest report of evaporation using an electron beam as the heating source was in 1934 by H. M. O’Bryan²⁷³ who noted that evaporation from filaments and crucibles available at the time was limited by restrictions to relatively low melting point evaporants and the tendency of many materials to alloy with the heating element. He developed a technique for evaporating refractory materials such as boron, boron carbide, silicon carbide, molybdenum, platinum, and chromium utilizing a high-purity (“spectroscopic purity”) graphite crucible heated by an electron beam from a coiled tungsten filament.

O’Bryan noted that a “disadvantage” of this technique is that a vacuum of 10^{-5} Torr is required (two to three orders of magnitude lower than was commonly used at the time).

He also pointed out that the electron-beam current should be maintained low until the filament itself, as well as the crucible and evaporant, are outgassed. Finally, he introduced the use of a tantalum radiation shield around the electron-beam filament to decrease heating of, and tungsten deposition on, the system walls. This system was the forerunner of the modern “e-beam” evaporator,²⁷⁴ Figure 42, in which the electron beam is electromagnetically focused in a 270° arc and rastered over the evaporant surface to uniformly melt a region in the middle of a solid chunk of the evaporant material contained in a water-cooled copper jacket. Thus, contamination is minimized as the solid evaporant material serves as its own crucible.

a. Reactive evaporation. Most of the early researchers in evaporative metal film deposition were actually doing reactive evaporation, although not on purpose, due to the high background gas partial pressure of oxygen water vapor, etc. Irving Langmuir, in 1913, was perhaps the first to report experiments focused in a purposeful way on deposition by reactive evaporation of a gas-metal compound in high vacuum. He heated tungsten wire above $\sim 2425^\circ\text{C}$ in nitrogen at pressures P_{N_2} up to ~ 100 mTorr and noted that P_{N_2} decreased due to the formation of tungsten nitride [W_2N] condensed on the glass walls of the system.²⁷⁵ He reported that N_2 disappeared from the gas phase at a constant rate, as monitored by a McLeod gauge (Sec. III E), until saturating at a minimum value. In an experiment with an initial N_2 pressure of 6.5 mTorr, the pressure was reduced to 0.1 mTorr in about 25 min. Reactive film formation in this case was a sidelight to the study of internal getter pumping for efficiently removing reactive gases from a vacuum system, an approach initiated in 1907 by Frederick Soddy (see Sec. IV B 4).²⁵⁶

Sustained investigation of reactive evaporation for film growth, driven by applications for thin oxide layers, did not occur until several decades later, in the 1950s and early 1960s. Max Auwärter of Balzers, Liechtenstein, filed a U.S. patent application June 19, 1953 (granted January 5, 1960),²⁷⁶ on high-vacuum reactive evaporation of metal oxides for optical films. (A related Austrian patent, 192650, was issued to Auwärter in 1952.). Using titanium dioxide [TiO_2] as the primary example, he describes evaporating Ti, or $\text{Ti} + \text{TiO}_2$, pellets from a tungsten (or molybdenum) boat in oxygen pressures P_{O_2} ranging from 4×10^{-4} to 7×10^{-3} Torr, depending upon the evaporant source composition and the direction of O_2 flow, to obtain films which

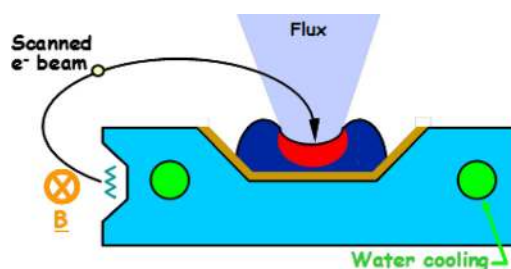


FIG. 42. Schematic illustration of a modern electron-beam evaporator (courtesy of Angus Rockett, University of Illinois at Urbana-Champaign). See text for description.

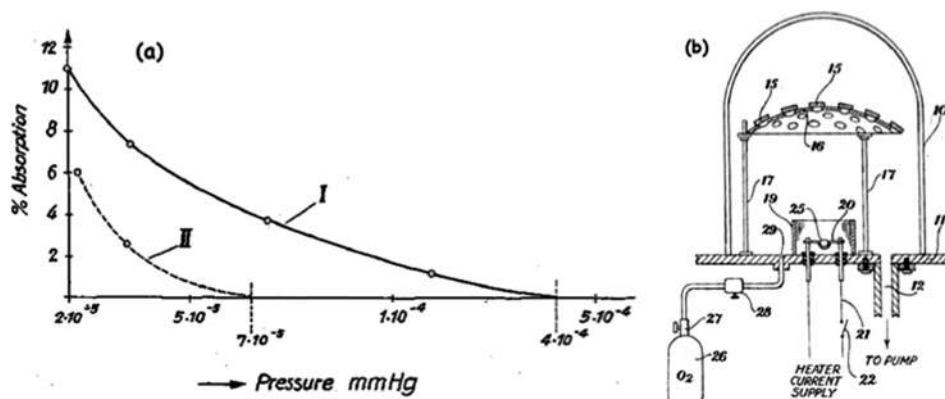


FIG. 43. (a) Measured absorbance of TiO_2 films deposited by reactive evaporation in pure O_2 with gas flow orthogonal to the evaporation direction (curve I) and parallel to the evaporation direction intersecting the substrate surface (curve II). Adapted from Ref. 276. (b) TiO_2 reactive evaporation chamber design showing a large concave substrate holder in which many glass substrates can be coated per deposition cycle. Adapted from Ref. 278.

were highly transparent in the visible. A feedback system, consisting of a vacuum gauge controlling a needle valve at the gas inlet, was used to maintain the O_2 pressure constant.

Figure 43(a) is a plot of Auwärter's results for film absorbance vs. P_{O_2} with O_2 gas flow parallel to the direction of evaporation (curve II) and intercepting the substrate. Curve I shows that flowing the gas in the opposite direction, parallel to the substrate surface, requires higher P_{O_2} values to achieve the same film transparency. Auwärter also noted that P_{O_2} can be decreased even further by ionizing the gas in a small glow-discharge chamber prior to introduction into the evaporator. He shows designs for discharge chambers with, and without, magnetic field support. While not discussed by Auwärter, the glow-discharge was effective in increasing the oxygen incorporation probability in growing films by cracking O_2 molecules to produce O atoms which are much more reactive. The patent preceded by two decades the development of what is now termed activated reactive evaporation (ARE) by Rointan Bunshah (University of California at Los Angeles) and colleagues in 1972.²⁷⁷

Doris Brinsmaid and colleagues at Eastman Kodak Company also filed for a U.S. patent on the reactive evaporative deposition of TiO_2 , six weeks before Auwärter, and patent 2,784,115 was issued March 5, 1957.²⁷⁸ The Kodak approach was quite similar, although Brinsmaid preferred the use of pure Ti, rather than a mixture of Ti + TiO_2 , as the evaporant source and thus required somewhat higher P_{O_2} values. She does point out that setting the O_2 pressure too high results in oxidation of the Ti source material to form a slag which is difficult to evaporate. The patent also notes that both the positions at which the reactive gas is introduced, closer to the substrates is better, and the flow pattern are important. The latter was also pointed out by Auwärter. However, Brinsmaid's patent goes a step further to describe a ring-shaped shower head reactive-gas distributor, with holes facing the substrates, to provide more uniform delivery of O_2 over a large concave (presumably stainless-steel) substrate holder (see Figure 43(b)) which allowed many glass substrates to be coated per deposition cycle. Brinsmaid also discussed the use of a motor-driven "cam-shaped" mask designed to provide better film thickness uniformity.

Elmar Ritter²⁷⁹ at Balzers showed that the oxygen pressure P_{O_2} required to deposit under-stoichiometric silicon oxide SiO_x ($x < 1.5$) films at room temperature is lower if the evaporant source is silicon monoxide [SiO], which

evaporates non-dissociatively, rather than pure Si. For films with higher O/Si ratios, there is no significant difference (see Figure 44). However, these early results clearly demonstrate that increasing x from 1.5 to the stoichiometric SiO_2 value, $x = 2$, requires a very large increase in P_{O_2} for both cases, graphically highlighting the important result that the O_2 reactive sticking probability decreases dramatically as x approaches stoichiometry. That is, O_2 molecules react with available pairs of neighboring Si atoms, via second-order kinetics, not with islands of SiO_2 .

b. Evaporative web coating. As noted in Sec. IV B 1 b, the first commercial web coaters, in 1934, utilized sputter deposition to deposit gold on glassine to produce metal foil for hot stamping in specialty printing processes. Another early web coating application in the mid 1930s, developed in this case by engineers at Bosch (Germany), was metallizing paper to produce capacitors consisting of wound dielectric paper tapes with vacuum-evaporated band-shaped zinc electrodes.²⁰⁸ Device failure due to electrical overload caused the paper to burn locally and the adjacent electrodes to short-circuit. However, Bosch researchers discovered that if the zinc thin film electrodes were less than $0.1 \mu\text{m}$ thick, the

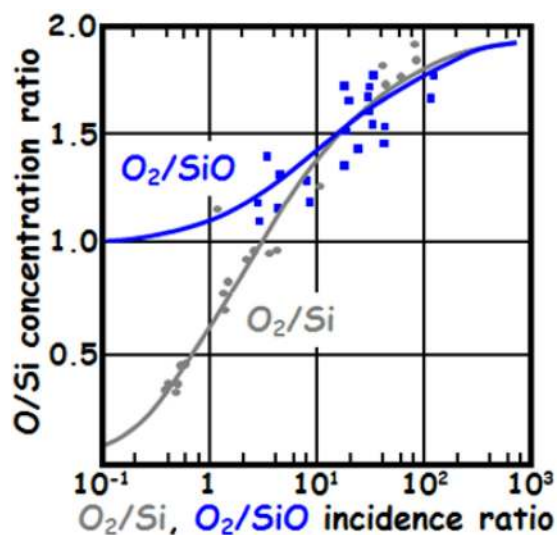


FIG. 44. SiO_x film composition, O/Si, vs. the incident O_2/Si and O_2/SiO flux ratios during reactive evaporation from Si and SiO source materials in pure O_2 . Reproduced with permission from E. Ritter, J. Vac. Soc. Technol. 3, 225 (1966). Copyright 1966 American Vacuum Society.

metal around the capacitor-break vaporized as the paper burned and the dielectric loops were again insulated from each other and functional. This was advertised as a “self-healing” effect, once again portending modern thin film technology.^{280–282}

In web coaters, a continuous flexible substrate is introduced via an unwinding mandrel, coated, and then taken up on a winding mandrel; thus, the term roll-to-roll coating (today, “R2R”). Problems with residual moisture emanating from the unwinding web quickly led to the design of multi-chamber systems, with separate pumping for each module to ensure a sufficiently low pressure in the deposition chamber. Figure 45 illustrates the first commercial system, consisting of four chambers, for producing paper capacitors with evaporated metal electrodes.²⁰⁸

c. Back to surface science. In a remarkable set of papers, Irving Langmuir demonstrated that previous interpretations explaining the absence of thin-film deposition on glass substrates at room temperature, and slightly lower, during evaporation of high-vapor-pressure metals as being due to atomic reflection were incorrect.^{232,262,283} Robert Wood had reported, for example, that when vacuum-evaporated mercury atoms impinge on a glass substrate cooled by liquid air (boiling point ~ 78 K, -195 °C), a film was formed; however, no film was obtained on glass at room temperature.²⁸⁴ In another series of experiments, vacuum-evaporated cadmium atoms did not form a film unless the glass substrate was cooled below -90 °C. However, if cadmium islands are formed at low temperature, film growth continues even after the glass substrate is heated to room temperature.²⁸⁵ Wood explained the second set of results by concluding that cadmium atoms condense on cadmium surfaces at room temperature, but are reflected by glass surfaces except at very low temperatures.

Langmuir argued that in fact the thermal accommodation probability (the probability that an incident atom loses that component of its excess kinetic energy orthogonal to the surface) was essentially unity in all of the above experiments (the atoms were *not* reflected).^{232,262,283} (It was shown much later, both by modeling and experiment, that the accommodation probability is high, approaching unity, even for rare-gas atoms incident at room-temperature metal surfaces.)^{286,287} Thus, essentially all incident metal atoms in Wood’s experiments were “condensed” (Langmuir’s terminology) at the substrate surface, irrespective of the temperature. However, at room temperature on glass, the atoms re-evaporated

(desorbed) at high rates. Today, surface scientists further distinguish between condensation and chemisorption probabilities.²⁸⁸ The former is the likelihood that a thermally accommodated atom also loses the parallel component of its incident kinetic energy during surface migration to a chemisorbed (chemically bonded) site, rather than desorbing.

Langmuir explained Wood’s cadmium pre-nucleation experiment results by first noting:²⁸³

“When a thick evaporated film of cadmium is heated above its melting point [321 °C], the molten cadmium gathers together into little drops on the surface of the glass. In other words, the molten cadmium does not wet glass. [Thus, the surface tension of cadmium is higher than that of glass, see Sec. III D.] Therefore, cadmium atoms have a greater attractive force for each other than they have for glass. Thus, single cadmium atoms on a glass surface evaporate off at a lower temperature than that at which they evaporate from a cadmium surface. It is not unreasonable to assume that in Wood’s experiments, even at -90 °C, the cadmium evaporated off of the glass as fast as it condensed upon it.... Atoms striking a surface have a certain average “life” on the surface, depending on the temperature of the surface and the intensity of the forces holding the atom.”

Langmuir explained the Cd pre-nucleation results without the benefit of modern nucleation theory. In addition, he added yet another important insight: namely, that the incident deposition flux J_i , at a given substrate temperature, also plays a key role in determining the lifetime of deposited atoms on the substrate surface.²⁸³

“Each atom of cadmium, striking the glass at room temperature, remains on the surface for a certain length of time before evaporating off. If the pressure is very low, the chance is small that another atom will be deposited, adjacent to the first, before this has had time to evaporate. But at higher pressures this frequently happens. Now if two atoms are placed side by side on a surface of glass, a larger amount of work must be done to evaporate one of these atoms than if the atoms were not in contact. Not only does the attractive force between the cadmium atom and the glass have to be overcome but also that between the two cadmium atoms. Therefore, the rate of evaporation of atoms from pairs will be much less than that of single atoms. Groups

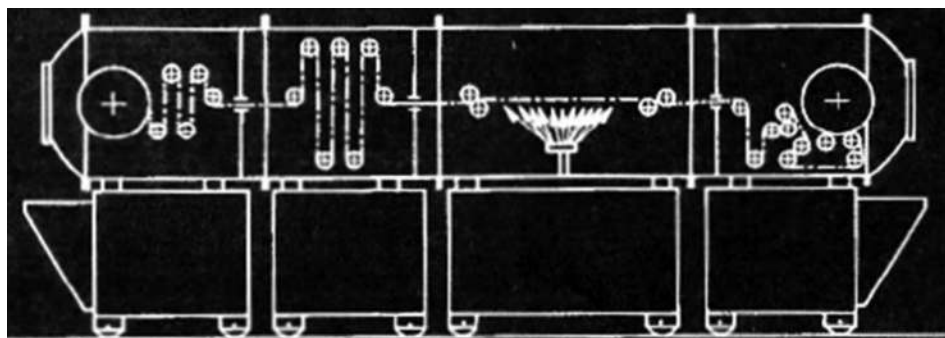


FIG. 45. Illustration of a four-chamber, separately pumped, evaporative roll-to-roll web coating system developed by Bosch (Germany) in the mid 1930s to deposit zinc electrodes on paper capacitors. Adapted from Ref. 208.

of three and four atoms will be still more stable. Groups of two, three, four, etc., atoms will thus serve as nuclei on which crystals can grow.”

Thus, the use of pre-nucleation is one more technological breakthrough that we attribute to “modern” thin film science, but was discovered, and understood, almost a century ago. A related technology, the use of an interfacial adhesion layer during thin film formation, was discovered by the Egyptians ~5000 years ago (see Sec. II), and pre-deposition of an adherent metal seed layer (by arc evaporation and latter sputtering) prior to electrodeposition onto phonograph records was patented by Edison in 1892 (Sec. IV B 1).

Langmuir advanced his ideas an important step further when he derived, in 1918, the equation which is now commonly referred to as the Langmuir isotherm,²⁸⁹ a thermodynamic equation of state which expresses the dependence of the equilibrium coverage²⁹⁰ of deposited atoms (or molecules) on a solid surface as a function of the atom pressure (or incident atom flux J_i), the adsorption rate constant, and the desorption rate constant. The latter two terms vary exponentially with temperature.

V. CONCLUSIONS: THE PRESENT GOLDEN ERA OF THIN FILMS

Inorganic thin films have had a remarkable history stretching over at least 5000 years. Interest in these materials has ranged from curiosity to practical uses to experiments to scientific understanding to the development of controlled and sophisticated deposition techniques to modern devices. One measure of success is the fact that a significant fraction of the modern literature in this field is concerned not just with the science of thin films, but with practical applications which enhance the quality of our daily life.

We are presently living in the third, and perhaps the most exciting and stimulating, golden age of thin films. As opposed to the first two eras, we now have available an incredibly powerful suite of characterization tools which allow us, with atomic resolution, to chemically identify and follow the dynamics and reactions among single and small groups of atoms and molecules on pristine atomically flat regions of a solid surface. In addition, materials modeling, simulation, and theory, exhibiting ever better agreement with experiment, are being developed at an increasing pace. Moreover, there are very strong commercial driving forces that lend confidence that the third thin-film golden age will continue into the foreseeable future. Examples include the following.

- * Economic: thin films dramatically reduce the volume of expensive materials used in essential applications; e.g., gold films for nanoelectronic ohmic contacts and conducting stripes, platinum films (and gold nanoparticles) for catalysis,²⁹¹ and silver films and nanoparticles for antimicrobial medical and water-purification applications.^{292,293}
- * Weight: the use of thin films, rather than bulk devices and sensors, is essential in, for example, space deployment.
- * Tuning materials properties: thin films provide a much more convenient experimental platform than bulk

materials, due in large part to the much higher diffusivity of adatoms than bulk atoms, for tuning materials properties via control of, for example, grain texture, phase transitions (e.g., surface-initiated spinodal decomposition can be initiated at temperatures far below those required for the corresponding bulk materials),^{294–296} and the growth of artificial materials (e.g., superlattices)^{297–299} and metastable phases^{300–302} with unique properties not found in nature, while exhibiting high-temperature stability.

- * New device functionalities: due to both semi-classical (high surface-to-volume ratios) and quantum confinement effects.

A primary goal of modern thin film science is to synthesize artificial materials with atom-by-atom control in order to achieve unique sets of desired properties not found in nature. The thin film and nanoscience communities are clearly making significant progress in that direction. Once again, however, the ancients anticipated “modern” science. Democritus (~430–370 BC), a pre-Socratic Thracian philosopher living in what today is northeastern Greece, proposed that all matter is composed of atoms (the word “atom” is derived from the Greek word *atomos* meaning uncuttable, indivisible) and that the strength of a material derives from interactions among constituent atoms.^{61,303} In 415 BC, he reminds us that “Nothing exists except atoms and empty space, everything else is opinion.” This remains good advice in 2014 as we ponder the future of atom-by-atom thin film synthesis. Finally, lest we take ourselves *too* seriously, it is also useful to consider another famous quote of Democritus: “Everything existing in the universe is the fruit of chance and necessity.”

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