5

ELECTROLESS AND ELECTRODEPOSITION OF SILVER

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Silver metal has been known since ancient times. It is mentioned in Exodus and Genesis. There exist strong indication that man was able to separate silver from lead as early as 3000 BC. Silver may be found native and in ores. Lead, lead zinc, copper, and other ores are principal sources. Silver may also be recovered during electrolytic refining of copper. Pure silver has the highest electrical and thermal conductivity of all metals. It retains that property in the form of electroplated thin film as well. This makes electroplated silver an important component of many printed circuit systems.

There is indication that silver was plated as far back as the beginning of the nineteenth century. If correct, it must have been done in connection with producing mirrors. The earliest patent for silver plating, however, was not granted until 1840 [1]. That may be viewed as signifying the start of the electroplating industry. That bath is still one of the more used ones to this day, and it is the double-silver cyanide complex [$KAg(CN)_2$] with excess free cyanide. Over the years many other baths have been proposed [2], such as the ones involving nitrate, iodide, thiourea, thiocyanate, sulfamate, and thiosulfate. The usages of silver plating are many. Those include mirrors and deposits for tableware due to its decorative effect as well as resistance to corrosion in its contact with foods. There are a number of industrial uses as well. Those include, but are not limited to, electronic component applications, bearings, hot-gas seals, to name but a few. Silver may be plated using either electrodeposition methods or electroless methods. We discuss here both methods, starting with the latter.

5.1 ELECTROLESS DEPOSITION

It is often necessary to silver coat insulators such as glass or ceramics. While a number of methods may be employed for this purpose (e.g., chemical vapor deposition, ion sputtering), chemical methods, and in particular the methods of electroless deposition, offer an effective, easy to operate path. In general, electrochemical methods may be classified into two types. One is galvanic exchange. Here the potential difference between metals is used to replace one metal layer with another (e.g., in "zincation"). The other is electroless plating where reducing agents are used. Electroless plating is the main focus in this presentation. As mentioned in a number of other chapters in this book, the electroless methods are effective because of the simplicity of the apparatus used, and they can be done on complex substrates; last, but not least, the methods are suitable for mass production.

5.1.1 Pretreatment

The substrate pretreatment for electroless silver plating involves, besides cleaning and degreasing, immersion in $SnCl_2$ solution and subsequent rinse in water. If, for instance, the substrate is glass, then the next step is immersion in the silver metallizing bath. Fine silver particles that are positively charged in solution will adhere to the glass surface, and the Sn^{2+} species will reduce the silver ions to metallic silver by being oxidized themselves to the Sn^{4+} state. Since silver is autocatalytic for the electrodeposition of itself, plating will continue as long as the substrate is immersed in the bath. For substrates other than glass, there will be the need to add the step of immersion in $PdCl_2$ before proceeding to the metallizing stage.

5.1.2 Metallizing Baths Compositions

In practice, the metallizing bath is made by combining two separate baths. One is a silver ion solution, while the other is

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a reducing agent solution. In what follows we will denote them as A an B, respectively.

1. Rochelle salt based [3] (most often used)
   A: Silver nitrate 450 g, saturated ammonia solution 350 mL water 5.5 L
   B: Rochelle salt 1600g Epsom salt, 110 g water 3.6 L
2. Glucose method [4]
   A: Silver nitrate 3.5 g, ammonia solution as required, water 60 mL, sodium hydroxide solution 2.5 g 100 mL^{-1}
   B: Glucose 45 g, tartaric acid 4g, water 1 L, ethyl alcohol 100 mL
3. Hydrazine method [3] (used for spray method, see below)
   A: Silver nitrate 100 g, ammonia solution (as required) 230 mL
   B: Hydrazine sulfate 43 g, ammonia solution 45 mL

In case 3, the A and B are diluted to 4.5 L and then mixed to the ratio 1 : 1.

5.1.3 Bath Properties

Electroless silver plating baths are very unstable and so short lived. It is desirable to stabilize the baths for electroless deposition of nickel and copper. In the case of silver this becomes imperative. Indeed, if the bath can be made more stable, it will be that much more useful. It has been found [5] that a small amount of 3-iodotyrosine or 3,5-diiodotyrosine added to a bath (referred to as DIT bath) can work as stabilizer.

There seems to be a strong indication that the electroless plating reaction progresses with a combination of a cathodic reaction of a cation, that is, $M^{n+} + ne \rightarrow M$, and an anodic oxidation of the reducing agent $R \rightarrow O + ne$. Here it is assumed that a metal ion is cathodically reduced to metal on the surface that is activated by a catalyst. This state of affairs is valid for silver as well as for other metals on which autocatalytic reaction will occur. A number of examples with representative reducing agents are given above. In all silver oxide precipitation is avoided because the electroless silver plating is carried out in a basic solution. The complexing agent is added to the solution.

Not at all surprising is the fact that bath stability and plating rate are markedly affected by the pH of the bath. Consequently the parameters affecting the bath pH were investigated [5], It was found, for instance, that the pH changes with the addition of silver nitrate. The change is most noted when the pH values are below 10.5. The complex formation between silver ion and ethylene diamine (en) is most likely as follows:

$$Ag^{+} + 2H_2O + 2en \leftrightarrow [Ag(OH)_2en_2]^{-} + 2H^{+}$$

Equilibrium consideration of the reaction indicates that the bath pH changes with concentrations of Ag^+ and en. Even in the case of a stabilized bath (using 3,5-diiodotyrosine), the plating reaction all but stopped after 24 h and the pH of the bath dropped. To clarify the foregoing, we present in Figure 5.1 the electroless plating rate of silver as a function of bath pH. From the figure it is evident that a slight drop in pH value may drastically reduce the plating rate.

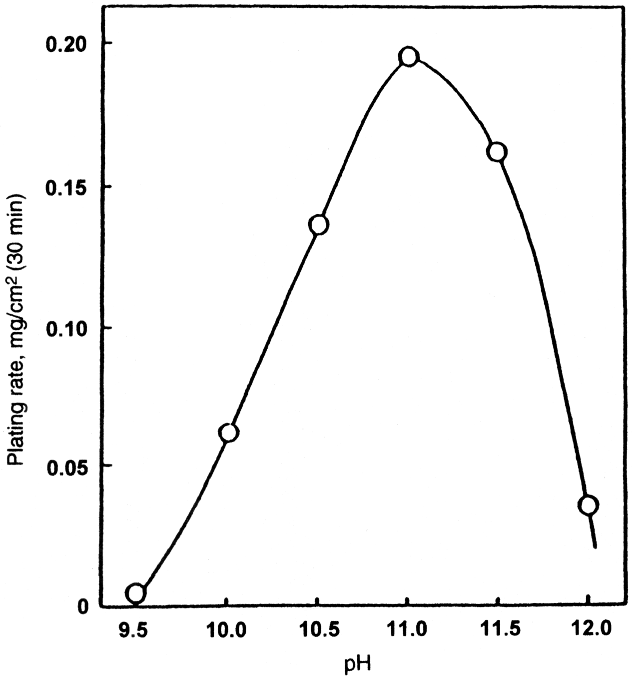

FIGURE 5.1 Electroless plating rate of silver as a function of bath pH: Silver nitrate $2.9 \times 10^{-3} M$, ethylenediamine $1.8 \times 10^{-2} M$, Rochelle salt $3.5 \times 10^{-2} M$, 3,5-diiodotyrosine $4 \times 10^{-5} M$, 35°C. Reproduced with permission of American Electroplaters and Surface Finishers, Inc. [3].

Other stabilizers have been reported in the literature. They include metal ions (Co^{2+}, Ni^{2+}, Co^{2+}) [6], Na-2-3-mercaptopropane sulfonate ($NaBH_4$, N_2H_4, CN^- system bath) [7], and a number more.

5.1.4 Polarization

The specific effects of pretreatment and the mechanism of silver plating can be inferred from the partial anodic and cathodic polarization curves [5]. Both the partial cathodic polarization curve for a solution without Rochelle salt as the reducing agent and the partial anodic curve for a solution without silver nitrate are given in Figure 5.2. In these the stabilized DIT bath was used. The result for the (electrode) surface pretreated with a $SnCl_2$ solution is shown by a solid line, while that for a nontreated one is shown by a dotted line. The difference between the partial cathodic polarization curves in Figure 5.2 is minimal. This is not so with the

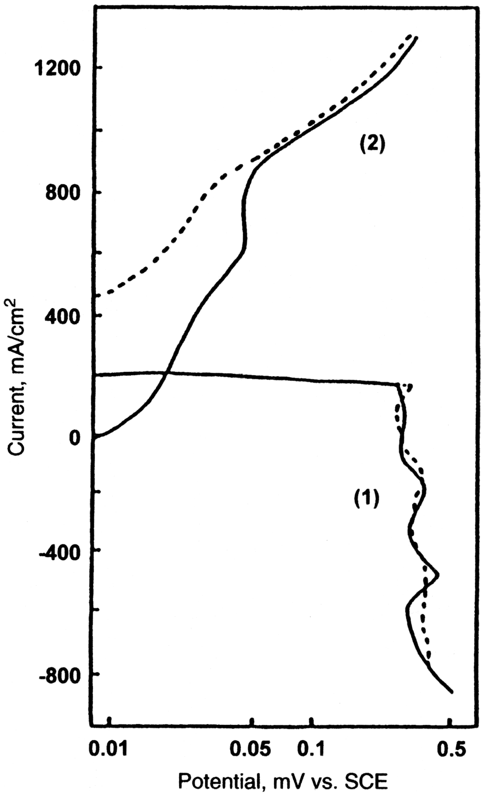

FIGURE 5.2 Partial polarization curves for various electrodes: (1) partial cathodic polarization curve of electroless silver plating solution without Rochelle salt—$AgNO_3$ (0.88 *M*), ethylenediamine (0.054 M), DIT (4×10^{-5}*M*), 3S°C, pH 10.0; (2) partial anodic polarization curve for electroless silver plating solution without silver nitrate—ethylenediamine (0.054 *M*), Rochelle salt (0.035 *M*), DIT ($4^{-5} \times 10^{-5}$*M*), 35°C, pH 10.0. (*Solid line*) Pt electrode sensitized with $SnCI_2$ solution; (*dotted line*) Pt electrode, not sensitized. Reproduced with permission of American Electroplaters and Surface Finishers, Inc. [5].

difference between the anodic polarization curves of the treated and the untreated electrodes being plainly evident. In the case of the treated electrode, an anodic current appears also in the range of 100–600 mV versus the saturated calomel electrode (SCE). At the same time the rest potential of the untreated electrode becomes 25 mV versus SCE while that of the treated becomes −81 mV versus SCE. The difference in the rest potential may be attributed to the adsorption of Sn^{2+} ions on the electrode. In other words, it is assumed that the anodic current due to oxidation of Sn^{2+} flows at potentials of 100–600 mV versus SCE. When the anodic and cathodic polarization curves for the treated electrodes are combined, a point of intersection appears at 0.02 mA cm^{-2} of current density. When this value of current density is converted to plating rate, it is found to be equivalent to 0.04 mg cm^{-2} over 30 min. This value is found to be close to the actual plating rate as determined experimentally. In the case of the untreated electrode, the current density at the intersection is extremely small. Thus, at least in the case of the DIT bath, it may be assumed that the electroless silver plating reaction proceeds only on the nucleation centers established by the $SnCl_2$ surface treatment and does not occur on the untreated surface.

5.1.5 Deposition in Practice

In the practical silvering operation the silver ion solution and the reducing agent solution are prepared separately. They are combined just before plating. Upon addition of the ammonia solution to the silver nitrate solution, a dark black-brown precipitate begins to form. The ammonia solution should be added until the precipitate all but dissolves. The solution ends up dark brown and clear.

In the spray method a number of different, specially designed guns [8] are used. One such gun has two tubes. The two solutions are sprayed separately and mixed on the substrate. There are a number of different final baths [5, 9–15] suggested in the literature, given at the end of this chapter.

Displacement methods [16] can be used in electroless silver plating on metal. For instance, the bath composition for silver plating on copper alloy is made of silver nitrate 7.5 g L^{-1}, sodium thiosulfate 100 g L^{-1}, and ammonia 75 g L^{-1}. There are many other formulations [17] given in the literature.

The applications of electroless silver deposits are many, but they may be divided into two categories:

1. Decorations and optical uses
2. Electrical conductivity and undercoating prior to other plating
3. Over coating in the process of manufacturing printed circuit boards

Mirrors [18] are an example of the first type, and undercoating for electroless gold plating or for silver plating on ceramics is an example of the second application type. One other important application is the plating of silver on ceramics for the purposes of SEM (scanning electron microscopy) measurements of surface properties [19]. Still other applications include quantitative analysis for trace amounts of arsenic [20], for the determination of pore diameter of a membrane [21], and for the recovery of mercury.

In connection with 3 above, it should be noted that the commercial process for depositing electroless silver uses an aqueous $AgNO_3$ solution in the presence of HNO_3 [22]. The manufacturers of printed circuit boards employ the electroless deposition of silver metal to prevent the degradation of exposed copper conduction tracks prior to the final assembly procedure of the devices (which can sometimes be up to several months). Of course, silver is much more susceptible to aerobic oxidation than copper; however, silver oxide and sulfide, along with underlying silver metal, are very soluble in the tin- and tin/lead-based molten solders that are used to bond the circuit components to the copper tracks of the circuit board.

The conventional processes use strong inorganic agents, such as HNO_3, that can etch the copper substrate, but as component sizes keep shrinking, the etching of the copper tracks during silver plating is becoming a serious problem for the electronics industry. More specifically, component failures can occur due to copper etching by the electroless bath before the surfaces have been silver plated. The work in [22] demonstrated that a sustained galvanic coating of silver can be deposited onto copper substrates from a solution of Ag^+ ions in an ionic liquid (IL) based on a choline chloride (ChCl) eutectic. The sustained, electroless but not autocatalytic growth of the silver deposit is facilitated by the porous nature of the film. This was proven using acoustic impedance spectroscopy on a quartz crystal microbalance (QCM). The silver and copper surfaces were characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM/EDX). In comparison, it should be stressed that in the commercial process of dip coating of silver from ions from aqueous media, deposition does not continue once surface coverage has been arrived at without the use of catalysts. The process referred to in this discussion using ionic liquids [23] produces silver deposits of several micrometers by dip coating without the use of catalysts or strong inorganic acids [24].

This section may not be considered complete without accurate general definition of the concept of ionic liquid. That is particularly true as the last decade or so has witnessed a growing interest in the field of ionic liquids. Ionic liquids are essentially low-temperature molten salts and as such are responsible for a wealth of intellectual and technological challenges as well as opportunities for the production of new chemical processes, fuel cells, batteries, and new composite materials (see, Chapter 30 in this volume and [25]).

5.2 ELECTRODEPOSITION

5.2.1 Bath Composition

The specific composition of silver (cyanide) plating baths has to fit the required silver plate. For instance, silver plate for decorative purposes is best achieved from baths with a lower silver content than those used for engineering purposes where thicker deposits are needed. Higher silver concentrations make higher current densities possible, and as a consequence more economic plating speeds can be employed.

It is worth noting out here that many present-day silver plating baths are similar to that described in the first patent over 150 years ago. Table 5.1 gives the silver deposition bath compositions that are in common use to date. Indeed, even a typical bath composition offered recently [26] in the literature for silver electroplating is made as follows:

TABLE 5.1 Typical Bath Composition ($g\,L^{-1}$)

	Bright Silver (Conventional)	High Speed (Thick Deposit)
Silver (metal)	20–45	35–120
Silver cyanide	31–55	45–150
Potassium cyanide (total)	50–80	70–230
Potassium cyanide (free)	35–50	45–160
Potassium carbonate	15–90	15–90
Potassium nitrate	—	40–60
Potassium hydroxide	—	4–30
Current density ($A\,dm^{-1}$)	0.5–1.5	0.5–10.0
Temperature (°C)	20–28	35–50

Note: Brighteners are added as required.

AgCN	0.0185 *M*
$K_4P_2O_7$	0.3027 *M*
KCN	0.1228 *M*

Such a bath may be operated at pH 10.8 with a value of −100 mV (vs. Ag) polarization.

A number of attempts have been made to replace AgCN and thus the cyanoargentite ions by different silver electrolytes based on nitrate (see Section 5.1 on electroless deposition), thiourea, and other compounds. These solutions, however, exhibit instability, and the resulting deposits are of low quality in terms of adhesion and the like. So cyanide solutions are used at the present time despite their toxicity. The only way to minimize the cyanide concentration is to employ a lower amount as the formulation in [26] suggests. This approach requires sophisticated deposition methods such as pulse plating.

5.2.2 About Bath Constituents

It is evident from the discussion above that alkaline silver cyanide provides the silver for deposition on the cathode. From a practical point of view low silver content and high free cyanide yields improved throwing power. On the other hand, higher silver concentrations allow the use of higher current densities. Thus for this reason baths low in silver content are used for deposits of thickness between 2 and 5 μm. The alkali cyanide increases the conductivity, and the cathode polarization provides good anode corrosion, not to mention its function in forming the silver complex ion. Also KCN and not NaCN is used because it induces higher solution conductivity, higher solubility of the resultant potassium carbonate buildup, and higher limiting current densities. Potassium carbonate too increases the conductivity of the bath and also the anode and cathode polarizations, which improves throwing power. The concentration of the carbonate rises with the decomposition of the cyanide. Thus initially the concentration added to the bath is kept to the recommended minimum.

Silver cyanide forms a complex $KAg(CN)_2$. One gram of AgCN requires about 0.5 g KCN in addition to the free cyanide indicated in Table 5.1. Over the years we have found that the most convenient way to prepare a tank full of silver plating bath is as follows: Dissolve the bath constituents other than the potassium silver cyanide and dissolve the possible brighteners in a separate container of water equal to about half of the bath volume. Heat the solution to about 70°C; the solution can be heated with the presence of activated carbon ($1.5\ g\ L^{-1}$). Stir until the constituents dissolve (about 40–45 min) and then filter it into the operating tank. Fill the tank almost to the full volume and then add the $KAg(CN)_2$ to the tank while stirring. This way no silver will be removed with the carbon. At this stage brighteners can be added and the tank filled up to the right volume. Now, at the risk of repeating what has already been stated above, we offer the following advice: Silver deposition is a well-studied technology in the area of metal deposition. While electron transfer to silver ion should be rapid, ideal silver surfaces may have slow nucleation, as shown by Budevski et al. [27]. For a majority of substrates and simple silver solutions, dendritic silver is produced through nucleation and three-dimensional (3D) growth of individual metal grains with little or no tendency to merge and compact. Thus, to obtain smooth deposits of silver, plating from cyanide complexes is practiced in most cases.

5.2.3 Anodes and Anodic Reactions

Cyanide silver plating baths are fairly stable and easy to maintain. Cathode and anode current efficiencies are close to 100%, and the solution can be kept in balance for long periods of operation. For this reason the use of high-quality silver anodes (purity of 99.98% or better) is recommended.

It may be useful at this point to elucidate the process of silver dissolution in cyanide solutions. Cyanide leaching, first introduced in 1887 [28], remains to this day the common means to recover gold and silver from ores. The reaction was recognized by early workers to be electrochemical in nature [29]. The kinetics of silver cyanidation has been widely studied, but very little has been said about the reaction mechanism. Vielstich and Gerischer [30], using the potential step method, verified the Butler–Volmer equation (see *Fundamentals*, Chapter 6, Eq. 6.45) with transfer coefficient α values of 0.5 and 0.44 for $[CN^-] > 0.2\,M$ and $< 0.1\,M$, respectively. The predominant complex ion of silver was assumed in their study to be $[Ag(CN)_3^{2-}]$, and it did not depend on cyanide concentration. Nachaev and Beck [31], on the other hand, studied the discharging of silver in cyanide solutions measuring the Faraday impedance. They found that through all potential values more negative than -0.45 V silver was deposited through the discharging of $[Ag(CN)_2^-]$ ions independent of the composition of the bath and the conditions of electrolysis.

It was found [32, 33] that a surface-enhanced Raman scattering (SERS) spectrum may be obtained from cyanide adsorbed on a silver electrode. As a result silver has been reaffirmed as an electrode of much interest. Lately a number of studies have concentrated on the method and efforts to correlate SERS with electrochemical methods prevail. For instance, voltammograms for the silver cyanide system with the corresponding SERS spectra of adsorbed silver cyanide were presented by Benner and co-workers [34]. Fleischman and co-workers [35] obtained SERS spectra of $^{12}CN^-$ and $^{13}CN^-$ adsorbed on silver electrodes. These spectra were shown to arise from a complex species whose coordination number did not change with the electrode potential. The species were proposed to be $[Ag(CN)_2^-]$. Blondeau and co-workers [36], using radiochemical means, found that after several dissolution redeposition cycles the quantity of cyanide adsorbed remained constant and the silver cyanide reaction was reversible. New information from SERS spectra prompted Baltruschat and Vielstich [37] to study the system again via potentiostatic pulse methods. Using the exact methods of mathematics rather than extrapolating, they obtained better accuracy for exchange current densities. Their results indicated that neither the anodic dissolution of silver in cyanide solution nor its reverse process involved simple charge transfer reactions: that is, (1) the reaction orders are not integers, (2) the apparent transfer coefficient is dependent on concentration or potential, and (3) the rate-determining step is not purely charge-transfer controlled. They also showed that pH has no influence on the process. A more recent work by Zhu and co-workers [38] is also of some interest. They point out that up to the early 1990s (1) research had focused on concentrated cyanide solutions (above $0.1\,M$), (2) the mechanisms require further clarification, (3) the combined effect of intrinsic kinetics and physical processes (e.g., diffusion) are yet to be measured, and (4) the adsorption of cyanide ions on silver surfaces is a steady-state phenomenon. Their work, in which electrochemical techniques were used to examine the kinetics of silver cyanidation in oxygen-free alkaline solutions, drew the following conclusions: The reaction between silver and cyanide may be separated into the two elementary steps: a charge-transfer reaction followed by a chemical reaction. Since the charge-transfer step, which includes the diffusion of cyanide ions from the bulk solution to the silver surface, is rate limiting, the rate of dissolution is calculated using the combined Butler–Volmer and Levich equations.

From the electrochemical measurements the diffusion coefficient of cyanide ions in $0.5M$ KNO_3 solutions (pH 11; $[Ag] = 5 \times 10^{-5}\,M$ and $[CN] = 5 \times 10^{-4}$–$1 \times 10^{-2} M$) is found to be $1.6 \times 10^{-5}\ cm^2\,s^{-1}$ at 24°C and the activation energy 13.7 kJ. The apparent exchange current density in the solutions has been concluded to have an activation energy of 21.1 kJ mol^{-1}. The transfer coefficient has been found to be close to 0.5, but it changes somewhat with temperature (between 0.56 and 0.43).

5.2.4 Deposition on Metals

The pretreatment of the metal surfaces that will be silver plated includes the standard steps of cleaning and etching to which is added a silver strike. The explanation for this additional treatment is that most basic metals are less noble than silver (as is even gold in the cyanide system). Consequently they will precipitate silver by immersion, from the regular silver plating baths, and cause the silver deposits to poorly adhere. The strike baths should contain low silver metal and high free-cyanide concentrations. In this way the tendency for electrochemical displacement by the base metal is greatly lowered. Besides, the process involves low-efficiency hydrogen activation. The procedure for steel surfaces is to use a double strike: the first in a solution containing low silver content with some copper cyanide and the second in a regular strike solution. The latter may be used as the first strike solution for copper, its alloys, nickel, and nickel silver. Solution compositions are given in Tables 5.2 and 5.3. The strike can also be used for surfaces made of more than one metal or with soldered parts. The recommended immersion times range from 10 to 25 s for decorative silver plating, while for thicker deposits it can range from 15 to 40 s. It is also recommended that the object to be plated be made cathodic before immersion in either the strike or the plating bath.

5.2.5 Additives

In general, small quantities of certain substances, mostly organic, can markedly affect the form or structure of the deposits. Since it can be assumed that adsorption takes place at the cathode surface during electrolysis, one added molecule affects many thousand metal ions. Often the added effects are undesirable. If, however, the result is a bright or level surface or if internal stress is reduced, the added substance is not considered a contaminant. A decrease in the activation overpotential is observed, for instance, for carbon disulfide in the cyanide silver bath. (The effect is the opposite in other metal's bath.) The subject of additives and their nature is discussed in detail in Chapter 10 of *Fundamentals*. For this reason we will only make a few general practical observations and leave it to the reader to consult that text.

TABLE 5.2 First Strike Bath for Steel

Silver cyanide	1.5–2.5 g L^{-1}
Copper cyanide	10–15 g L^{-1}
Potassium cyanide	75–90 g L^{-1}
Temperature	22–30°C
Current density	1.5–3.0 A dm^{-2}
Volts	4–6

TABLE 5.3 Strike for Nickel and Nonferrous Metals and Second Bath for Steel

Silver cyanide	1.5–5 g L^{-1}
Potassium cyanide	75–90 g L^{-1}
Temperature	22–30°C
Current density	1.5–3.0 A dm^{-2}

The susceptibility of the different metals to the inhibition of electrodeposition by many additives is nearly parallel to their melting point, hardness, and strength, increasing in this order: Pb, Sn, Ag, Cd, Zn, Cu, Fe, Ni. This sequence also fits the order of the increasing tendency of their ions to form complexes. The sequence further fits the order of increasing activation polarization in electrodeposition from their aquated ions.

The additives are generally consumed in the deposition process. They may be decomposed, and the products in parts incorporated into the deposit, or released back into the electrolyte. As a rule we note that they will affect the internal stresses in the deposits positively or negatively.

Carbon disulfide and thiosulfate have been widely used as additives (brighteners) in silver plating baths. A host of other materials have been used as well. Some are gums, sugars, unsaturated alcohols, sulfonated aliphatic acids, turkey red oil, rhodamine red, and compounds of antimony and bismuth. The majority are sulfur-bearing organic compounds or else reaction products of sulfur and organic compounds. There exist a good number of effective proprietary additives that yield highly desirable deposits in terms of mirror brightness. Such products, when available, obviate the need for buffing the final plate, which not only saves precious metal but also assures a more uniform thickness.

5.2.6 Physical Properties

One of the underlying concepts of thin-film science is that of surface energy (SE). This is the energy required to create a surface. Interestingly metals, as a rule, have a high SE, while oxides have a low SE. The relative values of SE determine whether one material wets another and thus forms a uniform adherent layer as required in the case of electroplated metal. Material with low SE will tend to wet a material of high SE. Conversely, if the deposited material has a higher SE, it will tend to form clusters; that is, it will "ball up" on the low-SE substrate. Water proofing is a way of manipulating surface energies. Organic materials tend to have low SE; thus a car waxed with an organic substrate will

TABLE 5.4 Relationship between Surface Energy and Latent Heat

Metal	Surface Energy (erg cm^{-2})	Latent Heat Evaporation (kcal mol^{-1})	Ratio SE/LH	Interatomic Potential (eV atom^{-1})	Cohesive Energy (kcal mol^{-1})
Copper	1700	73.3	0.22	0.58	80.4
Silver	1200	82	0.15	0.65	68
Gold	1400	60	0.24	0.47	87.96

cause water droplets to form on its wet surface. As stated above, SE is defined as the energy spent to create a surface. It is a positive quantity, since energy is added to the system. A liquid balls up to reduce its surface area, and crystals will facet in order to expose their lowest energy surfaces. When one breaks a solid, two new surfaces are created and bonds are broken. It should thus be clear that SE is related to bond energy and to the number of broken bonds creating surfaces. This dynamic in turn is related to the binding energy of the material.

The binding energy is defined as the energy needed to transform one mole of solid or liquid into gas at a low pressure. That is nearly the same as the energy of sublimation (transforming solid to gas) or the energy of evaporation (transforming liquid to gas), except that the gas is measured at the pressure of one atmosphere rather than at low pressure. These energies are related to the interatomic potential energy between atoms.

Using "nearest-neighbor-only interaction" approximation, we are able to relate the heat energy of sublimation, evaporation, melting, and crystallization to surface energies. The binding energy per mole of a substance is expressed as

$$E_b = \tfrac{1}{2} n_c N_A \varepsilon_b$$

where n_c = coordination number, which is the number of nearest neighbors
A_A = Avogadro's number
ε_b = binding energy per single bond

The factor of $\frac{1}{2}$ comes as a result of having counted bonds twice.

To evaluate surface energy from the point of view of nearest-neighbor bonds, we first define N_S to be the number of atoms per unit area and E_S/A to be the surface energy per unit area. Across any atomic plane each atom has an average $n_c/2$ nearest neighbors, so the number of bonds to be broken per unit area of cleavage along the plane is $1/2 n_c N_S$. Now, since we create two surfaces in cleaving, the surface energy per unit area is $n_c N_S \varepsilon_B$. Finally, the ratio of SE per atom to binding energy per atom, $1/4 n_c \varepsilon$, is given by

$$\frac{E_S/AN_S}{E_B/N_A} = \frac{1/4 n_c \varepsilon_b}{1/2 n_c \varepsilon_b} = \frac{1}{2}$$

From measured values shown in Table 5.4, we can calculate the ratio of surface energy per atom to bond (or latent heat, LH) per atom. Indeed, from the table we can infer whether it is easier to deposit silver on copper or whether it is easier to deposit copper on silver.

Silver metal is noted for its extremely high electrical conductivity, $0.0162\ \Omega\text{-cm}^2\,\mathrm{m}^{-1}$. It is somewhat unique in that even in its thin-film form it exhibits nearly the same property, 0.017–$0.024\ \Omega\text{-cm}^2\,\mathrm{m}^{-1}$, depending on deposition conditions and additives. For instance, sulfur and selenium containing electrolytes yield deposits with conductivities of up to 90% that of bulk silver metal.

Another physical property of importance in the case of electrodeposits is microstructural instabilities due to creep (relief) of stress with ensuing time. An optically flat mirror made of silver deposit will deform in a matter of a few months. This is due to room temperature relief of stress in the silver electroplate. Brass mirrors made optically flat and subsequently silver plated show deformation as a result of stress in the silver plate. Removing the silver by machining will restore the original flatness of the brass. Heat treating the silver-plated part at 150°C for 1 h seems to eliminate the problem.

5.2.7 Fractals

In general, electrodeposits made using baths containing no additives are dendritic or treelike. These types of deposits are of no practical value. In recent years these types of deposits contributed to the study of fractals. A fractal is an object with a pattern that under magnification exhibits repetitive levels of structures; a similar structure exists on all levels. In other words, a fractal looks the same whether it is viewed on the scale of a meter, a millimeter, or a micrometer. In the human body, for instance, fractallike structures make up the blood vessels, nerves, and so on. In nature, coastlines and tree branching are the obvious examples. In the material sciences, the importance of fractals is that it leads the way to the study and quantitative analysis of the microstructure of metals in fashion hitherto thought impossible. Kahanda and Tomkiewicz [39], for instance, undertook the issue of fractality in regard to the impedance of electrochemically grown silver deposits. (See references

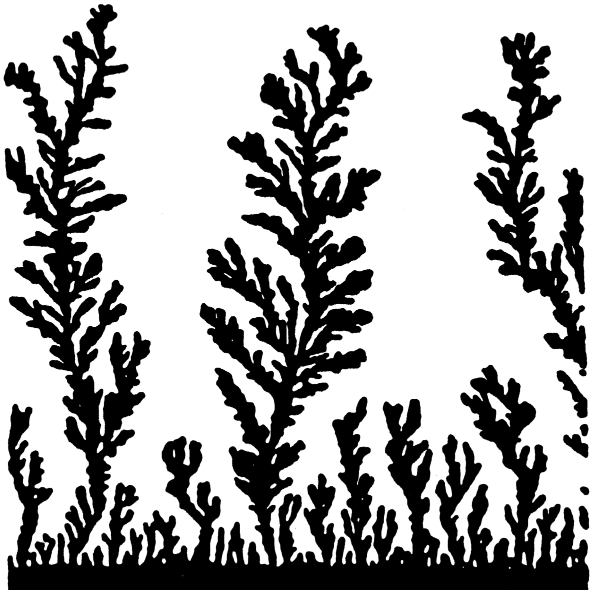

FIGURE 5.3 Electrodeposited clusters (about 0.5 cm in length) photographed 15 minutes after start of growth. Reproduced with permission of The Electrochemical Society [39].

in [39] regarding fractals in general.) To illustrate the fractal nature of some electrodeposits, we present in Figure 5.3 a photograph of metal clusters obtained after 15 min in a bath with no additives.

REFERENCES

1. G. Elkington and H. Elkington, British Patent 8447 (1840).
2. S. R. Natarajan and K. Krishman, *Met. Finish.*, **50** (2), 51 (1971).
3. S. K. Gupata, *Cent. Glass. Ceram. Res. Int. Bull.*, **14**, 18 (1967).
4. T. Ishibashi, *Less Met. Finish.*, **9**, 42 (1968).
5. A, Kubota and N. Koura, *J. Met. Finish. Soc. Jpn.*, **37**, 131, 694 (1986).
6. T. Hata and T. Hanada, U.S. Patent 3,337,350 (1967).
7. A. Vaskelis and O. Diemontaite, *TSR Mokslu Akad. Darb.*, **B4**, 23 (1975).
8. I. Cross, *Met. Finish*, **48**, 77 (1950).
9. S. Noguchi, Japan Patent 7,593,234 (1975).
10. S. Horst, German Patent 2,063,334 (1972).
11. T. Mukaiyama, Japan Patent 7,216,819 (1972).
12. S. Werner, German Patent 2,639,287 (1978).
13. Max Ernes, German Patent 950,230 (1956).
14. D. J. Hood, U.S. Patent 2,120,203 (1938).
15. Y. Mori, Japan Patent 7,606,135 (1976).
16. T. Kanabe and M. Ise, *Ind. Met. Sur.*, **7**, 64 (1979).
17. B. A. Bochkarev and E. Z. Napukh, *Elktrokhimia*, **18**, 6, 843 (1982).
18. G. Maurice, German Patent 2,153,837 (1971).
19. V. J. Pakolenko, *Zanod. Lab.*, **48**, 10, 89 (1982).
20. L. V. Markova, *Z. Anal, Khim.*, **25**, 8, 1620 (1970).
21. K. Wekua and B. Hoffman, *Furbe u. Lack*, **58**, 250 (1952).
22. A. P. Abbot, J. Griffith, S. Nandhra, C. O'Connor, S. Postlethwaite, K. S. Ryder, and E. L. Smith, *Surface Coating Technol.*, **202**, 2033 (2008).
23. K. J. McKenzie and A. P. Abbot, *Phys. Chem., Chem. Phys.*, **8**, 4265 (2006)
24. A. P. Abbot, G. Capper, D. Davies, and R. K. Rashid, *Inorg. Chem.*, **43**, 3447 (2004)
25. K. E. Johnson, *Electrochem. Soc. Interface*, **16**, 38 (Spring 2007).
26. H. Sanches, E. Chainet, B. Nguyen, P. Ozil, and Y. Meas, *J. Electrochem. Soc*, **143**, 2799 (1996).
27. E. Budevski, W. Bostanoff, T. Vitanoff, Z. Soinov, A. Kotzen, and R. Kaischev, *Phys. Status Solidi.*, **13**, 577 (1966).
28. J. V. N. Dorr, *Cyanidation and Concentration of Gold and Silver Ores*, McGraw-Hill, New York, 1936, Ch. 1.
29. V. Kudryk and H. H. Kellog, *J. Metals*, **6**, 541 (1954).
30. W. Vielstich and H. Gerischer, *Z. Phys. Chem.* (new series), **4**, 10 (1955).
31. E. A. Nachaev and R. Yu. Beck, *Electrokhimia*, **2**, 150 (1966).
32. A. Otto, *Surf. Sci*, **75**, L392 (1978).
33. J. Billman, G. Kovacs, and A. Otto, *Surf. Sci.*, **92**, 153 (1980).
34. R. E. Benner, R. Dornhouse, R, K. Cheng and B. L. Laube, *Surf. Sci.*, **101**, 341 (1980).
35. M. Fleischman, I. R. Hill, and M. E. Plembe, *J. Electroanal. Chem.*, **136**, 361 (1982).
36. G. Blondeau, J. Zerbino, and N. Jaffrezic-Renault, *J. Electroanal. Chem.*, **112**, 127 (1980).
37. H. Baltruschat and W. Vielstich, *J. Electroanal. Chem.*, **154**, 141 (1983).
38. X. Zhu, J. Li, D. M. Bodily, and M. E. Wadsworth, *J. Electrochem Soc.*, **140**, 1927 (1996).
39. G. L. M. K. S. Kahanda and M. Tomkiewicz, *J. Electrochem Soc.*, **137**, 3423 (1990).