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Chapter 2

Electroless Deposition of Nanolayered Metallic Coatings

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Additional information is available at the end of the chapter

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Abstract

Electroless metallic coating is referred as the deposition of a substrate material by the process of chemical or autocatalytic reduction of aqueous metal ions deposited to a substrate material without any external supply of power. Electroless nickel alloys are generally considered synonymous to the word "*electroless coating*" as ~90% of productions in industries are of this alloy coating. Rest of the electroless metallic coatings includes gold, copper, palladium, cobalt, silver, etc. These electroless metallic coatings (other than electroless nickel coatings) are also one of the vibrant areas in the field of materials properties and surface engineering research. From the year 2000 to till date, nearly 1000 SCI indexed research papers were published on this topic. However, no comprehensive studies about the recent progress on this topic were reported elsewhere so far. In this context, the present chapter aims to give a complete overview on various aspects of the rest of the electroless metallic nanocoatings/layer as a whole. More importance will be on the recent developments of the nanocharacteristics and future scopes.

Keywords: electroless deposition, metallic coating, electroless nanocoating, electroless gold, electroless copper, electroless palladium, electroless cobalt, electroless silver

1. Introduction

The term "Electroless coating" is referred to as the reduction of aqueous metal ions plated to a substrate by autocatalytic or chemical means, in the absence of external current [1–3], and it disregards the technique used to perform coating in the absence of current such as immersion plating (deposition of copper on steel dipped in copper sulfate solution or nickel on steel dipped

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in chloride and boric acid bath) and the process of homogenous chemical reduction (silvering). The mechanism of autocatalytically deposited electroless metallic coatings differs in a way completely from coatings obtained by immersion plating or silvering, wherein in the latter case, nature of base material itself will behave as a reducing agent and does not necessitate any external reducing agent to initiate any metal ion to metal reduction. However, these processes have not gained wide acceptance, as it has poor adherence and non-productive behavior. Electroless process has received widespread acceptance in the market due to their exceptional anti-corrosion [4–6], wear resistance properties [3, 5–7] and also good for soldering and brazing applications [8]. Many metals like nickel, copper, gold, silver, palladium and cobalt are being deposited employing this technique [3, 9–12]. Rest of electroless coatings includes gold, copper, palladium, cobalt and silver [13–15]. These metallic coating/ layers (other than electroless nickel) are also one of the vibrant areas in the field of materials properties and surface engineering research. This review chapter provides an insight into the electroless metallic gold, copper, palladium, cobalt, silver, aluminum and the new processing technology in deposition mechanism and nanocharacteristics. Besides, more stress has been laid to understand the recent developments and its future scopes.

1.1. Historical overview

The term "electroless plating" also defined as "autocatalytic" is nearly as old as electroplating. Von Liebig first described it in 1835 with the reduction of silver salts by reducing aldehydes. In 1988, metallic nickel deposition by electroless technique from an aqueous solution in the existence of hypophosphite (reducing agent) was first stated as a chemical tragedy by Wurtz [3, 16]. Roux, in the year 1911, positively reported that there was clear precipitation of metal in the form of powder. However, these workings were not practically used for any applications. Development in this field did not receive much of patronage until World War II. The method established by Brenner and Riddell for coating a layer of nickel-tungsten alloy in the inner parts of tubes by means of a citrate based bath containing an insoluble anode yielded the hypophosphite with uncommon reducing properties. The Patent Office of US declared that this patent, issued in 1950, is distinct and varied from the earlier patent owned by Roux, in which the process was unstructured and complete. In contrast, Brenner and Riddell's method was described as a controlled catalytic process as deposition process took place only on catalytically active surfaces dipped in the plating bath. Dr. Brenner later manifested that his patent was an unintended outcome comparable to the efforts of Wurtz and Roux. But he added that the patent was taken in order to safeguard US government rights. Actually, in 1963, a publicized US Army based technical report was printed that pronounced mostly about the work of Wurtz and Roux and gave much of the finding credit to Brenner and also covered by patent in 1956 [17]. This phenomenon ascribed to the action of chemical reduction of nickel ions was later identified.

After initiation of electroless nickel deposit, rest of electroless coatings was followed. In 1970, semiconductors and circuit boards were plated with thick, pure soft gold after the development of the first electroless gold coating bath at Bell Laboratories [14]. Narcus first reported the electroless copper deposit, and the first profitable application was realized by Cahill and Zeblisky et al. [18] in tartarate baths, where the reducing agent used was formaldehyde. Improved formulations of electroless copper [19] recorded a higher rate of plating with exceptionally stable conditions under diverse operating conditions. Baum et al. developed a process for selective deposition of copper by first selectively depositing palladium seeds in

1986. Palladium and alloys of palladium have been identified as a pecuniary alternative to applications involving gold plating. Electroless cobalt discovered along with nickel deposition by Brenner and Riddell [1–3]. This technique of electroless cobalt deposition has been exploited frequently for the preparation of magnetic films. In particular, thin films of cobalt have found application as recording media on account of their thinness, high coercivity, and high remanence. The commercial application of electroless silver was developed early in 1970 [20]. Electroless aluminum [21], electroless platinum [22], electroless ruthenium, and electroless rhodium were developed. In the early 1984, materials like plastics; ceramics, polymers and other non-conducting materials are coated by electroless technique before even being subjected to electroplating. This phenomenon led to the development of the rest of electroless metallic deposits. Meanwhile, the field of electroless coating chemistry has materialized as one of the promising and key areas of the surface engineering and metal finishing research, etc.

1.2. Primary aspects of electroless metallic coating

The basic elements of any electroless bath and their role are briefly reported in **Table 1**. A typical electroless gold, copper, palladium and cobalt plating baths available in literature are illustrated in **Table 2** [3, 23]

Components	Functions
Metal ions	Source of metal
Reducing agents	Source of electrons to reduce the metal ions
Complexants	Stop excess of free metal ions concentration
Accelerators	Quicken the reducing agent and increase the deposition
Stabilizers	Mitigate the bath from decomposition by protecting catalytically active deposition
Buffers	Endure the pH for long time
pH regulators	pH tuning
Temperature	Energy to the bath deposition

Table 1. Electroless bath components and their functions.

Electroless bath	Gold	Copper	Palladium	Cobalt
pH, temperature and deposition rate	10–13, 65–85°C and 2–5 μm/h	9–13, 25–70°C and 1–5 μm/h	8–12, 45–75°C and 2–5 μm/h	9–14, 85–95°C and 2–10 μm/h
Metal salt(s) or Source	Gold chloride, Gold cyanide, Potassium aurate.	Copper sulfate, Copper carbonate, Copper formate, Copper acetate, Copper nitrate.	Palladium chloride, Palladium bromide.	Cobalt sulfate, Cobalt chloride.
Reducing agent(s)	Dimethylamine (DMAB), Sodium hypophosphite, potassium borohydride, Potassium cynoborohydride.	Formate, Formaldehyde, DMAB, Sodium hypophosphite.	Sodium hypophosphite, DMAB, Triethylamine borane.	DMAB, Sodium hypophosphite.

Electroless bath	Gold	Copper	Palladium	Cobalt
Complexing agent(s)	Potassium citrate, sodium phosphate, sodium borate, Potassium tartrate.	Rochelle salt, Ammonium hydroxide, pyridium-3-sulfonic acid, Potassium tartrate, Quadrol, EDTA.	Ammonia, Methylamine, EDTA.	Sodium citrate, Succinic acid. Ammonium chloride, Citric acid.
Stabilizer(s)	Alkali metal cyanide, Alkali hydrogen, fluoride, Acetyl acetone.	Thiodiglycolic, Thiourea, Sodium cyanide, Vanadium pentoxide, Potassium ferrocyanide, MBT.	Thioorganic compound. Thiourea, Organic cyanide, Thiocyanates.	Urea, Thioorganic compounds.
pH adjuster(s)	Potassium hydroxide, Phosphoric acid, Sulfuric acid.	Hydrochloric, Sulfuric acids, Sodium and Potassium hydroxide.	Ammonium hydroxide, Hydrochloric acid.	Ammonium hydroxide, Sodium hydroxide.
Major applications	Integrated circuit, chips, connector, and semi-conductor devices in electronic Industry.	Conductive layer prior to deposit on plastics or non-metallic, Printed circuit board and decorative purpose.	Printed circuit board, electronic switch contact, and it are alternative for electroless gold.	Magnetic memory disc and storage devices in electronic industry.

Table 2. Plating bath composition of typical electroless gold, copper, palladium, and cobalt with their major applications.

In the process of electroless deposition, the reduction of metal ions to metal takes place by the action of reducing agents, which are basically donors of electrons. The metal ions act as acceptors of electron and are subject to chemical reaction with the electron donors. This process is autocatalytic in which the acceleration of electroless chemical reaction subjects the reducing agent used to oxidize. The experimental apparatus shows the basic illustration of the setup usually used in experiments of electroless coatings (**Figure 1**). In addition to the basic setup, ultrasound improved the benefits in the electroless nickel, copper and cobalt plating [24].

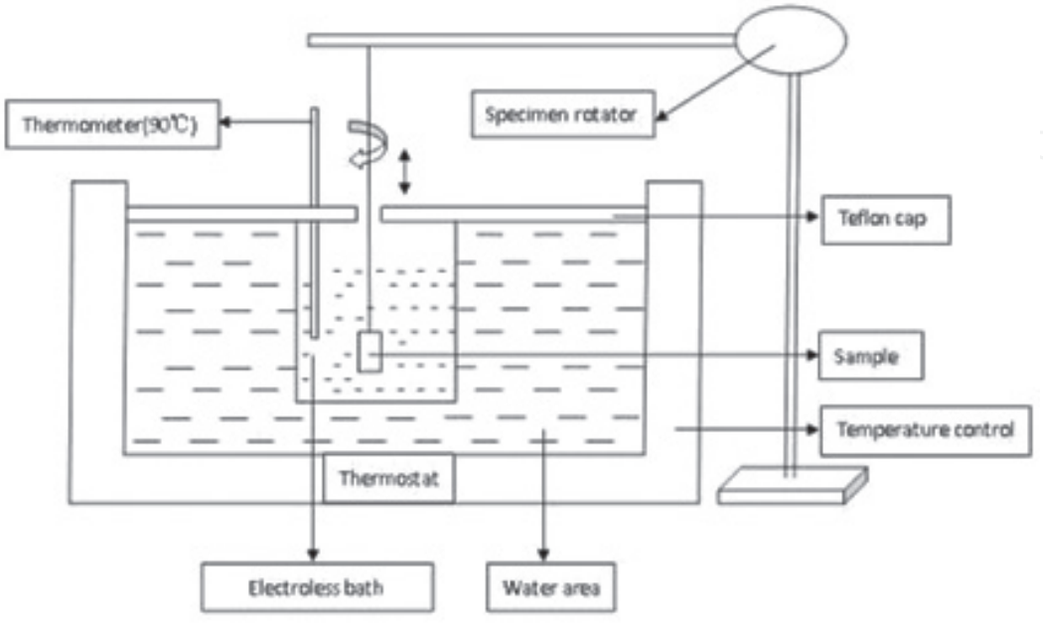


Figure 1. Basic illustration of the apparatus used in electroless coating experiments.

2. Rest of the electroless metallic coatings

2.1. Electroless gold

In most of the existing practices of electroless gold, coatings are produced initially by depositing a thin layer of immersion gold, followed by electroless gold plating [14, 15]. However, there are several shortcomings which depict electroless gold processes: (a) low deposition rates, (b) necessity to carefully regulate plating conditions, (c) substrates should be meticulously cleaned, (d) plating baths are likely to have relatively short lives, (e) stirring. Electroless gold deposition has been most successfully accomplished using a gold sulfite and ammonium salts of sulfite. Those salts of gold comprise of potassium gold chloride, gold cyanide and gold sulfite among which the most commonly used source is potassium gold cyanide. The reducing agents essential for electroless plating are as varied as the potential gold salts. A wide variety of reducing agents required for electroless are available as various potential gold salts such as sodium hypophosphite, dimethylamine borane, sodium borohydride, and hydrazine. It has been serving as the primary application for electronic industry to perform selective plating, thereby conserving plating costs and improve circuit design in integrated circuits [25]. There are some realistic cases of autocatalytic processes of coating gold with the ability of having achieved 99.99% purity. **Table 3** gives a typical bath composition for the electroless gold plating. Electroless plating of gold salts on germanium results in morphologically complex nanostructure metallic films [26]. Deposition simply takes place by means of galvanic displacement without the presence of pH adjusters, fluoride, complexing agents, or other external reducing agents. This facile method gives good control over deposition rate and surface morphology by proper variation of coating parameters such as temperature, immersion time and metal ion concentration. The preparation of Au nanowires of high aspect ratio by employing electroless reduction of gold in the hexagonally ordered, thiol-modified nanosized channels [27]. The outcomes evidently display that the development of the Au nanowires is templated by the channel structure of the base substrate. Ecofriendly electroless plating bath was developed by chloroauric acid ($HAuCl_4$) and hydrogen peroxide (H_2O_2) for depositing a film of gold onto (3-aminopropyl)-trimethoxysilane (APTMS). It could prove as a feasible replacement of using hazardous source of potassium gold cyanide [28].

Electroless gold bath composition	
Gold hydrochloride trihydrate	0.01 M
Sodium potassium tartrate	0.014 M
Dimethylamine borane	0.013 M
Sodium cyanide	400.0 mg/L
pH (adjusted with NaOH)	13
Temperature	60°C

Table 3. A typical electroless gold bath.

The various characteristics of electroless gold coatings attained from baths of borohydride have been abridged by Feldstein [29], and it is given in **Table 4**. This table shows mainly the physical properties of the gold plating (i.e., adhesion, density, porosity, and resistivity)

2.1.1. Recent developments of electroless gold

Electroless gold layer was developed on hydrogen-terminated Si substrate from aqueous hydrofluoric solutions [30]. The Au deposition is kinetically inadequate by diffusion at first, but then development of Au clusters is kinetically restricted by a surface reaction containing a fluoride species. This possibly necessitates for Au to be coated in a relatively mobile state initially which is only moderately discharged. Hou et al. reported about the preparation of gold films and affirmed the possibility for them to subsequently be used as base materials to aid the formation of self-assembled monolayers (SAMs) from alkanethiols [31]. The formation of SAMs on the films of electroless gold can be ascribed to two primary reasons. Firstly, any type of wet-chemical laboratory can be used to prepare electroless gold. In addition, electroless gold can be coated on intricate and complicated shapes of substrate, wherein no technique for the evaporation process could be recommended. The densely packed SAMs (prepared from hexadecanethiol), present on the surface of electroless gold, are only deposited as a thin film of evaporated gold. Electroless coating promoted the epitaxial growth of Au (111) on a seed layer of evaporated gold that makes it highly beneficial for microfabrication applications [32]. Wang et al. [33] have recently found that electroless Au microelectrodes could be fabricated on polycarbonate microfluidic chips with SAM, after cleaning the microelectrodes with plasma. The system comprised of a polycarbonate microfluidic chip with an electrochemical detector, a gravity pump, and an automatic sample loading and injection unit. Lei et al. [34] reported the analysis of prepared gold films with a surface plasmon resonance (SPR) device to detect the rapid and label-free detection of the white spot syndrome virus (WSSV). This method, key issues in the field of pisciculture and environmental toxicology, has been addressed and supplemented the expansion in the range of applications of the SPR technology. Schwarz et al. have recently [35] deposited a thin layer of soft gold onto polypyrrole and copper-coated paraaramid

Property	Value
Adhesion	Excellent on metals
Appearance	Matt yellow
Density	Bulk gold (19.3 g/cm^3)
Hardness	Soft (Knoop 60–80)
Porosity	~Zero for deposits, ≥ 1 μm on uniform substrate
Resistivity	Bulk gold (0.03 ohm/square at 1 μm)
Purity	99.90%
Thermo compression bond ability	Excellent

Table 4. Properties of electroless gold deposits.

yarns. Copper ions go into the solution as less noble copper dissolves, and consequently, there is a reduction of gold ions in the solution thereby getting deposited on the yarn surface. Once a thick layer of gold has been deposited, further dissolution of copper cannot happen and the process of charge exchange gets stopped. As gold layer is now formed on the yarn surface, autocatalytic chemical reduction takes place, and deposition continues further. Result revealed that the electroless coated yarns exhibited improved mechanical properties plus excellent electrical conductivity and considerable resistance to washing. Also, electrochemical results displayed that the gold coated yarns can be used to measure biomedical signals as they are promising electrode materials. An effective and simple electroless deposition technique was proven to deposit mixed SnO_2-Pd-Au film for sensing hydrogen. Electrical conductivity of the film was improved by the co-deposited gold. The sensor was easy-to-use and can be fabricated easily. This sensor can be used in areas like hydrogen gas alarm in commercial or domestic security [36]. Conducting electroless gold pads on light-emitting diodes chips are fabricated which exhibit no color difference, reliable wire bonding ability, and high values of electrical conductivity. The hardness of pads formed by electroless plating is three times softer than those formed by evaporation and the force gauges [37]. The industrial application of this plating is feasible.

2.1.2. Nanocharacteristics of electroless gold

The procedure for fabricating high-yield integrated nano-gap electrodes concurrently on a single sample was developed, which contains iodine solution (usually known as tincture (a medical liquid)) and ascorbic acid [38]. Results revealed that methods like nanogap fabrication and the fabricated gold nano-gap electrodes are beneficial for realizing applications like mono-electron and molecular nanodevices. Ding et al. have [39] produced Au nanoparticles using conducting polymer nanoparticles through electroless collecting $[AuCl_4]^-$ from solutions. A considerable improvement of the recovery capability of Au was realized by the polypyrrole nanoparticle when compared to the film or polypyrrole powder, due to the high specific surface area. Researcher [40] investigated in wielding electroless plated Au as a provision for carbon nanotube (CNT) electrodes. Further, they stressed the need for developing electroless techniques to meet the requirements of creating a more heterogeneous, uniform layer of gold to reduce desorption of cysteamine monolayer. An innovative nanotemplating technique was established to produce spherical gold nanoparticles (NPs) or regular arrays of silane rings on silicon substrates through selective electroless plating on layers of particle-lithographed silane [41]. This novel nanotemplating method can synthesize even and smooth metal NP arrays over huge areas to enhance the potential of improved spectral features in opto-plasmonic devices in spite of disregarding the requisites of large and expensive lithography and metal coating equipment. Research [42] defined a new electroless technique of depositing single-crystalline Au-NPs on and inside an organic single-matrix (SM) confined with both a stabilizer and a reducing agent. This process is appropriate for direct deposition of mechanically stable and optically transparent Au-NPs on and inside a SM. The development of palladium and platinum nanoparticles was made possible only with this method when the actual reaction was carried out on the surface of the SM in the presence of some gold nanocrystals.

2.2. Electroless copper

Electroless copper deposits have found their greatest applications for imparting a conductive layer for non-conductors before being coated by electrolytically. Electroless copper solutions resembling today's technology were first reported in 1957 by Cahill with the report of alkaline copper tartrate baths using formaldehyde as reducing agent. The pH range of 12.0–13.0 is generally optimal in formaldehyde-reduced baths. Formaldehyde-reduced electroless copper bath is given in **Table 5**. In printed-circuit boards industry, copper is deposited on the inner wall of the insulating hole that connects the two sides of the substrate by employing plating-through-hole process, one of the techniques of electroless copper deposition. Electroless Cu plating is becoming attractive because of its favorable nature of electrical & thermal conductivity, ornamental surface and so on [15].

Among the various chelating agents in electroless Cu plating (ethylenediamine tetraacetic, triethanolamine, and ethylenediamine), studies recognized ethylenediamine as an outstanding grain-refining agent owing to its strong adsorption on the Cu surface [43]. Formaldehyde is the reducing agent used in the great majority of commercial electroless Cu baths and other reducing agents have also been used successfully. The copper deposit increases the surface roughness by using pyridine-2,6-dicarboxylic and 4-hydroxypyridine-2,6-dicarboxylic acids as Cu (II) ions ligands in formaldehyde having alkaline electroless Cu plating baths [44]. The surface roughness factor (i.e., ratio of real surface area (nano-scale roughness) to geometrical surface area) was found to be the highest for pyridine-2,6-dicarboxylic acid having solutions at pH 13.

2.2.1. Recent developments of electroless copper

One of the most important applications of electroless copper is the electronic industry. The electroless Cu/Ni/Au deposits had the attributes of excellent adhesion in addition to having a low sheet resistivity, which are prerequisites for low attenuation at microwave frequencies. The above coating has been recommended as a cost effective means for microwave components because the thickness of gold in the proposed system is much less than that of conventional chromium/gold. Researcher studied the effective acceleration of deposition of copper at a temperature range of 20–30°C by a factor of 2–4, even for lesser additions of

Electroless copper bath composition	
Copper salt as Cu^{2+}	1.8 g/L
Rochelle salt	25 g/L
Formaldehyde as HCHO	10 g/L
Sodium hydroxide	5 g/L
2-Mercaptobenzothiazole (MBT)	<2 g/L
pH	12
Temperature	RT

Table 5. A typical electroless copper bath.

ammonia (1–3 mM) [45]. Acidic electroless Cu on aluminum-seeded ABS plastics was an alternative option for plating plastics, [46] and this was critically criticized because of its very slow rate. Hanna et al. [47] studied the role of various organic additives (cytosine, pyridine, benzotriazole and 2-mercaptobenzothiozole) which stabilized electroless copper baths in addition to enhancing the rate of plating. The bath stability increased 20 times to that of the aeration lacking-bath, as an effect of mild air agitation. This is an unusual method of non-isothermal deposition to enhance the deposition rate without affecting the plating bath. The deposition rate increased with increasing temperature of the substrate; nevertheless, the influence of bath temperature cannot be ignored. Result showed that this non-isothermal technique allows for deposition rates ~12 μmh^{-1} at certain conditions, which is 3 times than conventional isothermal method [48]. Recently, found long-term stability of Cu/Pd nanoparticles by using poly-vinyl-pyrrodione (PVP). In his study, acceptable activity and superior stability have been exhibited by the newly developed Cu/Pd colloidal system thus, indicating its capacity as an auxiliary for the prevailing Pd/Sn-based activator in PCBs [49]. The reduction of Cu(II) autocatalytically by formaldehyde from solutions having saccharose as the ligand initiates at a level of pH beyond 12, increases with an additional increase in pH, reaches a maximum value at pH 12.75, and then decelerates at higher pH values [50]. Tamayo-Ariztondo et al. [51] prepared electroless Cu deposits preferably on the surfaces parallel to graphene layers, due to the exposure of π bonds in the outside surface, and deposition was subdued on surfaces perpendicular to the graphene layers. Result revealed that there is maximum coverage of electroless Cu along the plane of graphene, and it is reduced at the edges of the plane. Garcia et al. [52] narrated two methods based on the ligand-induced electroless plating (LIEP) process to obtain patterns of Cu onto flexible polymer substrates. The LIEP process permits plating of copper selectively with stable electrical properties onto flexible polymer substrates. Therefore, the LIEP process collaborated with any of those patterning methods could perhaps be a better auxiliary for the classical processes of cost-effective fabrication of large-area plastic electronic devices and to endure substantial mechanical deformation with only a negligible loss in performance. Researcher developed activation for the dielectric surface by the cobalt compounds. This palladium-free activation looks hopeful for the practical application due to its stability and can be potential compare to many of the patented Pd-free activation solutions [53].

2.2.2. Nanocharacteristics of electroless copper

A research thrust has been initiated [54] that sub-100 nm copper films of low resistivity be deposited by electroless means on SAM of 3-aminopropyltrimethoxysilane and activated by 5 nm gold nano-particles. The resistivity achieved in this process is fairly relatable to the effective resistivity expected by the International Technology Roadmap for Semiconductors (ITRS) for realization in 2010–2011 years for 45 nm ULSI metallization. Noteworthy developments in wetting of aluminum can be attained by applying an electroless Cu on Al_2O_3 and SiC (Al/Cu-Al_2O_3 and Al/Cu-SiC) ceramics [55]. The copper coating present in the interface hindered the reactivity of SiC toward Al thus causing a clean interface. Recently, [56] a new method has been proposed to coat the surface of fly ash particles with conducting metal Cu by electroless, where titania/ultraviolet radiation/metal catalyst-system has been used instead of conventional Pd/Sn-based activator. More work has to be done, whether the proposed one

will be suit for the rest. Organic protection coatings act as an interlayer for highly reactive metals (magnesium) to coat electroless Cu and Ni or its alloys, and the process is criticized for its long time process. Daoush et al. studied on enhancing the strength of interfacial bonding between Cu and CNT by acid treatment and electroless copper coating of multiwall CNT to produce CNT/Cu nanocomposite powder with different CNT volume fractions. The electrical conductivity decreased, and the hardness increased with increase in volume fraction of CNT. The yield strength of the sintered materials had enhanced by increasing the volume fraction of CNT except in case of 20 vol. % CNT/Cu composite where the material fractured even before yielding. In addition, the increase in volume fraction of CNT in copper matrix witnessed an increase in Young's modulus and a subsequent decrease in elongation [57]. Wear and mechanical behavior of reinforced carbon nanofibers improved by electroless Cu alloy-based composites [58]. A new method proposed for plating a Cu layer onto an aramid film with a strong bonding by adhesion [59]. Deposition of electroless copper nanofilms on silicon and on polycrystalline germanium substrates seemed to cover an extensive area of the base material compared to other noble metals such as Au, Pt, Pd, and Ag [60]. Bruning et al. developed an in situ X-ray diffraction measurement for electroless Cu films. The strain evolution of films was determined based on three types of electrolyte. Within the experimental ambiguity, the correlation among stress and strain for the Cu films approves with the properties of bulk polycrystalline Cu [61]. The coating of Cu on particles of B_4C is required in order to synthesize metal-ceramic composites with improved sinterability and dispersability. A surface pretreatment similar to that of acid and alkali treated particles was carried out for B_4C particles. There was uniformity in the observed copper coating in alkali-treated particles at a level of pH-12, when matched to others. This is due to the effective elimination of impurities during the processes of production and processing of commercially existing B_4C [62]. The electroless Cu-P-SiC composite coating on carbon steel improved the anti-corrodibility behavior of deposits of electroless Cu [63].

Zangmeister and van Zee [64] observed the possibility of Cu to be deposited by the reducing action of formaldehyde on Cu^{2+} ions in 4-mercaptobenzoic acid SAMs, but inferred that the same cannot be performed on octadecanethiolate or 3-mercaptobenzoic acid SAMs. The formation of a surface-bound Cu complex when reduced by formaldehyde leads to the deposition of Cu metal. Garno et al. [65] observed another prospect for Cu to be deposited on COOH-terminated SAMs. Moreover, it was observed that smaller amounts of Cu could be deposited on CH_3-terminated SAMs, while narrowing likelihood of depositing Cu on OH-terminated SAMs. Recently, two main requirements for selective electroless deposition of Cu to take place were presented. Firstly, in cases where more than one type of functional group is present in the SAM, Cu^{2+} ions must interact with any one specific terminal group, if there is more than one group. Secondly, the temperature needs to be maintained adequately high to avert adsorption of non-specific Cu on non-interacting SAMs. It was significant, however, to maintain the reaction temperature in such a way, so that it was not too high to damage the SAM. The penetration of Cu into the Au/S interface through the monolayer was observed in addition to the deposition of Cu at the SAM/air interface. Moreover, the penetrating action through the SAM was noticed not to be ceasing even after plating was stopped [66]. This advises that electroless deposition of Cu taking place parallel with Cu evaporation may not

be an appropriate technique to develop Cu/SAM/metal or Cu/SAM/semiconductor junctions in molecular architectures based applications. This is because of the gradual shifting of upper Cu metal contact with respect to time. Alternative conditions of electroless deposition and metal types (e.g., Au, Pt, and Pd,) should be encouraged and moreover be explored to find the scope for formation of more stable metal over-layers with slight or without any metal atom penetration. Electroless Cu plating developed on nanofibers with the attributes of [67] high modulus and high strength, and particularly high electric conductivity on the surface of poly (p-) phenylene benzobisoxazole. A simple electroless Cu-coated prepared on glass nanofiber with excellent conductivity. Actually, this method is simple, low-cost, and large production and can be stretched to make other metal coated glass fibers by distinctive conductivity [68].

2.3. Electroless palladium

Palladium and palladium alloys can be deposited by the electroless mechanism using hypophosphite or hydrazine reducing agent. Palladium deposits find application in electrical contacts and connectors and serve as a diffusion barrier between metals such as copper and gold. It has been established as an economic substitute to gold plating. It has also been used as a best replacement for rhodium for wear application [69]. **Table 6** gives the constituents and composition details for an electroless palladium (hypophosphite-reduced) bath. The deposit can be hardened or be bonded to electroless nickel or be acquired with desired coating characteristics by means of varying specific bath components or their composition. For example, deposits with greater bond strength than the actual tensile strength of the palladium plate itself also can be attained. The plating can be direct in metals like stainless steel and nickel, whereas copper, brass, and other copper alloys would require an electroless nickel preplate.

The catalytic properties in Palladium have marked the metal notable in serving several applications of chemical and automotive industries. The usage of the metal is, however, been limited owing to high cost and difficulty to put it to realistic processing for other commercial applications. It is, yet, studied and proposed that thin films of palladium plated by electroless means onto ceramic sponge or other support materials may well be used effectually as reaction or auto emission catalysts. The metal and its alloys have been established as a profitable

Electroless copper palladium composition	
Palladium chloride	10 g/L
Rochelle salt	19 g/L
Ethylenediamine	25.6 g/L
Cool solution to 20°C (68°F) and then add:	
Sodium hypophosphite	4.1 g/L
pH (adjusted with HC1)	8.5 g/L
Temperature	68–73°C

Table 6. A typical electroless palladium bath.

substitute to gold plating. In spite of the differences in some of the properties of Pd and Au such as melting point and deposit hardness (**Table 7**), one character the metals share in common is the superior oxidation resistance.

2.3.1. Recent developments and nanocharacteristics of electroless palladium

It is often proposed that Pd/Sn-based activator is used to activate the substrate surface to deposit electroless Cu. In some cases, electroless Pd acts as an activator [70]. Recently, electroless Pd was coated on Iridium (Ir) and tungsten (W) substrates. The thickness of Pd was 20 and 30 Å on Ir and W substrates, respectively. A very strong adhesion of the electroless Cu to Ir and W was observed, when Pd was used as a catalytic layer [71]. In practical application point of view, modification of Pd by electroless on ZrO_2-TiO_2 selective layer produced membranes, which detached hydrogen and nitrogen gases in the Knudsen diffusion domain (H_2:N_2~3.75). In addition, using γ-aminopropyltriethoxysilane (γ-APTES) will ultimately lead to the proficient electroless deposition of amorphous and porous layers of Pd [72]. A method of vacuum electroless plating for synthesizing of thin dense Pd membranes on porous alumina tubes was developed. The diverse application of these membranes was ascribed to their high permeation performance, good thermal durability, and favorable chemical stability. Furthermore, these membranes had withstood tests for thermal durability over 470 h under H_2 or Ar atmosphere for both cycles of temperature cycles and gas-exchange. Additionally, these membranes offered a strong resistance to fluctuations in the chemical stability under various H_2 mixtures over a varied pressure and temperature range for 2000 h. No significant

Property	Electroless palladium	Electroless gold
Color	Silver/White	Yellow
Crystal	FCC	FCC
Resistivity	10.5×10^8 ohm-m	2.2×10^8 ohm-m
Magnetic	Paramagnetic	Diamagnetic
Density	12.0 g/cc	19.3 g/cc
Molecular weight	106	197
Melting point	1555°C	1063°C
Boiling point	3140°C	2660°C
Hardness	50–200 HV	20–150 HV
Elongation	24%	44%
Tensile strength	24 Ksi	18 Ksi
Co-efficient of expansion	6.5 μ-in./in./°F	7.9 μ-in./in./°F
Maximum thickness	Unlimited	Unlimited
Reacts with	HNO_3; HF	H_2SO_4; KCN; aqua regia

Table 7. A comparison between electroless palladium and gold.

changes in hydrogen permeation performance were observed, and sustained hydrogen permeation for the acute temperature fluctuations was exhibited. Another application oriented in electroless Pd membranes onto cordierite mini-channel network was developed recently and testified hydrogen separation [73]. Initially, the cordierite channels were coated in its interiors with alumina layers as supporting layers, consisting of a layer of micropowder alumina that covered a structure of bare cordierites structure of high porosity, and followed by a layer of nanopowder alumina resulting in an even surface free of defects for electroless plating of defect-free palladium films. The perm-selective palladium films fabricated in this new support structure also permits for extraction of hydrogen from hydrocarbon fuels in this design of integrated membrane reformers [74]. In some cases, the function of electroless Pd film on stainless steel is to increase the electrode potential and boost the rate of passivation of steel to endure strong corrosive environments [69]. Strukova et al. developed Pd-Au, Pd-Ag, Pd-Ni, Pd-Pb, and ternary Pd-Au-Ni alloy system onto different metallic substrates. The coatings of Pd-Au, Pd-Ag, and Pd-Ni have a solid solution structure, whereas Pd-Pb is intermetallic compound whose films after deposition comprised of nanocrystalline grains with sizes in the range of 11–35 nm [75]. Self-supported thin Pd alloys [76] membranes without defects were prepared for hydrogen permeation performance. The subsequent self-supported Pd membranes, less than 10 μm in thickness, demonstrate exceptional performance of hydrogen permeation and an extensive selectivity. In addition, a new type of non-alloy Ru/Pd composite membrane fabricated for hydrogen separation [77].

2.4. Electroless cobalt

Cobalt deposits are mainly produced from alkaline-hypophosphite baths. These coatings are produced from sodium hypophosphite-based solutions at a slightly alkaline pH range at elevated temperatures. The electroless cobalt deposition by hypophosphite is always supplemented by the co-deposition of phosphorus. The fabrication of magnetic storage devices with high area recording density generally requires magnetic material that is soft in nature. Its application includes large variety of magnetic properties and has found their major applications for switching and memory storage devices [78]. **Table 8** gives the information on constituents and composition of a typical electroless cobalt bath. Thin electroless Co deposits have their applications in the electronics industry (magnetic memory discs and storage devices) exclusively for

Electroless cobalt palladium composition	
Cobalt chloride	30 g/L
Sodium hypophosphite	20 g/L
Sodium citrate	35 g/L
Ammonium chloride	50 g/L
pH	9.5
Temperature	95°C

Table 8. A typical electroless cobalt bath.

their magnetic properties. In ternary Ni-Co-P alloy coatings, the Co content displayed a linear dependency with both pH of bath and temperature and was also influenced by the composition of Co sulfate in the electrolyte. It showed a spherical nodular structure with finer, compact grains and a homogeneous crystal structure. In addition, the maximum hardness was 804 HV_{50} for the deposits having 19% cobalt [79]. The maleic and succinic acid maintained the stability, long plating of the bath, and morphology of the as-plated deposits [80]. The deposition rate was more in the bath with succinic acid addition. These results are, though, inadequate for reporting evidences of electroless Co-based alloys with magnetic properties due to lack of systematic study on the conditions of preparation and intrinsic magnetic properties of the material.

2.4.1. Recent developments and nanocharacteristics of electroless cobalt

In Ni-Co-B ternary alloy coatings, the saturation magnetic moment was found to be increasing with rise in content of cobalt in the deposit and with prolonged annealing of the deposit [81]. SiC (Co-P-SiC) entrapment was more favored within the cobalt matrix composite coatings than Ni (Ni-P-SiC) matrix. The magnetic properties of the electroless Co-Fe-P films formed out of a stable sulfate bath [82]. In high pH bath with heat treatment films of Co-Fe-P, showed good soft magnetic properties. The magnetic properties of Co-W-P films have been studied by many authors [83–84]. Magagnin et al. [85] have proposed that electroless cobalt-phosphorus acts as a metallization barrier for copper in lead-free soldering. However, electroless Co-P/Au finish with about 4 wt. % P content sturdily restricts inter diffusion and formation of intermetallic compounds when paralleled to Ni-P/Au finish with Sn-Pb and Sn-Ag-Cu solder alloys. Furthermore, the shear test results suggested that Co-P/Au deposit having higher joint strength than Ni-P/Au deposit. Jiang et al. [86] have prepared SiC-W/Co nanocomposite particles by electroless cobalt on SiC whiskers. The bonding between the substrate and the cobalt coating is so weak due to which the thermal stability of SiC-W/Co composite is low. Hence, a research thrust has been initiated toward encouraging further investigation on the thermal stability of metal coating plated on whiskers. The electroless Co composites have not seemed to have received widespread attention and application; however, future prospects will be very attractive. The Co-Zn-P thin film coated nano-diamond materials were the basis for providing a feasible solution over the expensive cobalt material in the synthesis of this type of magnetic thin film materials. These magnetic film materials have been witnessing myriad prospective applications in the field of Magnetic Abrasive Lapping Materials in the near future [87]. CNT were decorated with FeCO using one-step polymer-stabilization activation step and low-cost electroless deposition. The approach recommends a viable method that can be followed for preparing nanoparticles of FeCo in application of cancer thermotherapy [88].

2.5. Electroless silver

Silver can be deposited from dimethylamine borane-based baths. The major application is to coat in the interior of waveguides. Many authors have reported and illustrated evidences of depositing electroless silver on different substrates. Abbott et al reported studies carried out about Ag coating on copper substrates using an ionic liquid [89]. A super hydrophobic surface formed by developing of a monolayer of polyfluoroalkyl thiol layer on copper or zinc substrate followed by electroless deposition of silver was reported by Larmour et al [90]. Various

methods for depositing silver on silicon substrates of definite patterns and plain Si substrate have also been recently explored [91].

2.5.1. Recent developments and nanocharacteristics of electroless silver

Electroless Ag nanoparticles were effectively deposited on ZnO nanorod surfaces for the purpose of decreasing the infrared emissivity values, due to its high reflectance and will lead to innovative options for producing materials of low infrared emissivity by doping metal to semiconductor materials. To impart electrical conductivity to non-conducting glass particles, possibility to deposit electroless Ag over the glass was reported to be feasible and efficient [92]. Electroless Ag was deposited on calcite and was first reported by Srikanth and Jeevanandam [93]. In their report, lower concentration of silver ions (e.g., 0.01 M $AgNO_3$) and shorter deposition times (e.g., 30 min) led to the formation of silver nanoparticles on calcite. Sun et al. [94] coated a uniform silver film about 50-nm thick on a graphite nanosheet surface by an enhanced electroless plating using 3-aminepropyltrimethoxysilane. This silver-coated graphite nanosheet exhibited high conductivity that was equivalent to that of the silver powder. There is still a need for new and simple methods for electroless deposition of silver metal on different substrates. A protocol was developed for a solid templating mask, which is utilized for the electroless modification of sulfate-terminated polystyrene spheres with caps comprised of silver nanoparticles. Miyoshi et al. developed an electroconductive Ag nanoarray on a Si wafer. The fabrication of nano-interconnections in electric circuits, nanowire grid polarizers, molecular sensors, and other functional devices has been attained with promising attributes of pattern and material variety on the scale of ≤50 nm for the above technique. Ag nanoparticles on hydrogenated SiN_x:H layers for photovoltaic applications. A novel activation procedure was developed, via electroless Ag deposition and comparable to the wet Sn-Ag activation. The investigated approach may find applications in the fabrication of metal microstructures and nanostructures on various substrates and is projected to have numerous applications in catalysis, plasmonic devices, sensors, and many other fields. Radke et al. successfully fabricated 3D metallic bichiral crystals via direct laser writing and electroless silver plating and this method exposes a route toward very complex 3D plasmonic structures in the optical range, for example, toroidal structures with completely unusual and novel types of optical resonances. Electroless Ag coating on tetraethoxy silane-bridged fiber glass has lowest electrical resistance of $1.56 \times 10^3\ \Omega/cm^2$ and good mechanical stability. Kim et al. developed uniform compact silver layer by ecofriendly electroless method on a $Fe/TiO_2/Ag$ core-shell structure [95–98].

2.6. Miscellaneous electroless coatings

2.6.1. Electroless aluminum

Electroless aluminum is capable of becoming one of the beneficial methods to develop thin films of Al and aluminum wiring at a very low cost. It is very difficult to perform electro deposition of aluminum in an aqueous solution because aluminum is not a very noble metal. In spite of being able to deposit Al from a room-temperature ionic liquid [99], there have been no established techniques well in virtue. A method used for the electroless plating of Al based on using $AlCl_3$-1-ethyl-3-methylimidazolium chloride ($AlCl_3$-EMIC) ionic liquid as the

electrolyte and lithium hydride (LiH) as the solid reducing agent. It is criticized for its bath composition (contained LiH) as it was challenging to control the bath condition and stability. The main reasons for the limited use of LiH-based baths are that LiH solubility in the plating bath is very low and usually supplemented with excessive temperature during the deposition reaction. Recently, the same group has further investigated electroless aluminum plating based on using $AlCl_3$-EMIC ionic liquid with di-isobutyl aluminum hydride (DIBAH) as a liquid reducing agent [100]. The DIBAH-based baths were easier to control and regulate for stability than that containing LiH. However, the reports on this topic such as film composition, plating condition, and reaction mechanism are still scarce. If the plating technique is established, it would widen the likelihood of obtaining thin and thick film coatings on the substrates of insulating material and intricate structures without electricity.

2.6.2. Electroless platinum and its alloy

Electroless bath and method of coating platinum and platinum alloys contain up to about 20% rhodium, up to about 10% iridium, and up to about 10% ruthenium on an active surface, wherein the bath is an alkaline solution containing about 2 to about 20 g/L of platinum, an alkali metal hydroxide to give a minimum bath pH of about 8, up to about 1 g/L of hydrazine. Electroless platinum deposits in the absence of the stabilizer have catalytic properties, whereas platinum and platinum alloy deposits in the presence of the stabilizer are bright. Electroless coating of platinum [101] group metals has reasonable descriptions on techniques for preparing solutions and setting up conditions of plating. However, all the information on individual processes was obtained only from the patent literature, and the basic interpretation of those processes is not well known. Besides, in a few exceptional cases, there are still lacunae about the detailed information on process characteristics and deposit properties.

2.6.3. Electroless ruthenium

Electroless ruthenium developed in a patent by using Ru-nitosylammine complexes with hyrazine. Hydroxylamine added to the bath acts as a stabilizer as it is generally done to the similar baths of electroless platinum. The baths contain both $[Ru(No)(OH)(NH_3)_4]^{2+}$ and $[Ru(No)(NH_3)_3]^{3+}$. The active ruthenium species are either added as their chloride salts or produced in-situ from other ruthenium salts, such as $RuCl_3$ or $K_2[Ru(No)Cl_3]$ with $NaNo_2$ and NH_4OH. The inventor found that the low operating temperature brands this process of ruthenium deposition highly suitable for materials that are mercurial at high temperatures [102].

2.6.4. Electroless rhodium

Electroless rhodium deposits were developed by Strejcek [103] by using hydrazine as the reducing agent. Rhodium bath solution: 0.1 g $RhCl_3.3H_2O$ + 100 ml water and a large excess of $NaNo_2$ (10 g). After heating in the range of 95–98°C for about 30 min, the color of the solution changes from red to pale yellow. After cooling, 5 ml of conc. $(NH_3)_n$ Rh $(No_2)_4$ a copper wire (with Al foil contacting) and a nickel sheet was immersed in this solution. With continuous agitation and heating, a 2% solution of $N_2H_4.H_2O$ was added drop wise. At 60°C, a bright deposit of rhodium was deposited.

3. Conclusions and future perspectives

The literature briefs and demonstrates the numerous attempts prepared to identify the interdependence of the parameters which influence the performance of electroless nanolayered metallic coatings (concentration, the problems, easier for the impending user to prepare a bath). There is scope for further research and empirical analysis to be done toward formulating a rest electroless plating bath that would be reliable for extensive application than the baths existing at present.

Simple work is needed to replace of using hazardous source of potassium gold cyanide in electroless Au layer coatings. Long-term stability of Cu/Pd nanoparticles requires lot of research, and more work has to be done, whether the proposed one will be suit for the rest. The thermal stability of SiC-W/Co composite layer remains less because of the weak bonding between the substrate and deposit. This Co composite seems to be inadequate, future prospects will be very attractive. This silver-coated graphite nanosheets exhibited excellent conductivity, equivalent to silver powder. Finding of new and simple approaches is needed for the deposition of silver metal on numerous substrates. If the electroless Al plating technique is established, it will be able to achieve the thin and thick film coating on the substrates of shielding material and complicated structures. The reports on this topic are still scarce. It was difficult to make critical judgment on the practical usefulness of electroless platinum and its platinum alloy. Nevertheless, future work is to improve the existing process as well as to develop new process useful for today's application.

It is expected that this review, together with the ideas proposed by the authors, will be helpful toward the development of newer practical applications. These studies have highlighted commercial viability for rest of electroless processes.

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