

Electrodeposition

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INTRODUCTION

Most important concepts and techniques of an electrodeposition are introduced and described here in an easy-to-understand way. Examples of technological applications are given, with emphasis on the fabrication of nanostructures.

DEFINITIONS AND HISTORY

Electrodeposition is an electrochemical process that allows the preparation of solid deposits on the surface of conductive materials. It is a commercially highly relevant process, providing the basis for many industrial applications, such as electro-winning, refining, and metal plating. Metal plating is the process that has perhaps the closest contact with most people's everyday life, because we are surrounded by things that have a protective or decorative coating, such as watches, buttons, belt buckles, doorknobs, handlebars, etc. Additionally and more recently, as will be seen below, not only do the circuit boards and the packaging modules of computers, but also the recording and reading heads of their hard disk drives and the micro-processor chip itself may have plated material on them.

Electrodeposits are formed by the action of an electric current passing in an electrochemical cell, a device that consists of two conductive or semi-conducting electrodes immersed in an electrolyte. The electrodes are called the working electrode (cathode), consisting of the object where electrodeposition is planned, and the counter-electrode (anode), necessary to complete the electrical circuit. Electrolytes for electrodeposition are usually aqueous solutions containing positive and negative ions, prepared by dissolving metal salts. The electric current that flows between the two conductive electrodes in the presence of an external voltage is because of the motion of charged species, via migration and diffusion, towards the surfaces of the polarized electrodes. At the surface of the electrodes, the conduction mechanism must change from ionic to electronic, an

interface process mediated by the occurrence of electrochemical reactions that promote the reduction or the oxidation (redox reactions) of the ionic species.

An electrochemical cell with a battery is illustrated in Fig. 1, where the motion of the ions toward the electrodes is also sketched. In this case, the metallic salt NiSO_4 (nickel sulfate) dissolved in water is a practical example of an electrolyte for Ni-plating metallic objects. In this example, the object to be plated is a key, placed as the working electrode. By applying an external voltage with the negative terminal of the battery connected to the working electrode, the Ni^{2+} move to this electrode, where deposition takes place, and the SO_4^{2-} toward the positively charged counter-electrode.

An essential characteristic of electrochemical reactions is that the exchange of charge does not occur between chemical species, as it does in a typical chemical reaction, but between chemical species and the electrode. The electrochemical reaction that is most important for the electrodeposition process is the one that occurs at the working electrode; i.e., for the example, in Fig. 1, it is the reduction reaction $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0$, where the Ni ions are reduced by receiving two electrons (e^-) from the electrode. At the counter-electrode, the oxidation of the sulfate radical is too energetic to occur, and the most probable oxidation reaction for inert electrodes in an aqueous electrolyte is the electrolysis of the water, forming H^+ and O_2 through the reaction $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^-$. This reaction occurs by donating two electrons to the anode, completing the electrical circuit and keeping the electric charge balanced. Frequently used inert electrodes include platinum and glassy carbon. If the counter-electrode is a metallic bar or foil (a non-inert electrode), the electrodisolution of the metal could provide electrons for the electrode and ions for the solution.

Historically, the discovery of electrodeposition is attributed to Luigi V. Brugnatelli, an Italian professor, who in 1805 was able to electrodeposit gold on the surface of a metallic object, from a solution containing dissolved gold, using a voltaic pile (battery). About 40 years later, John Wright, from Birmingham, England,

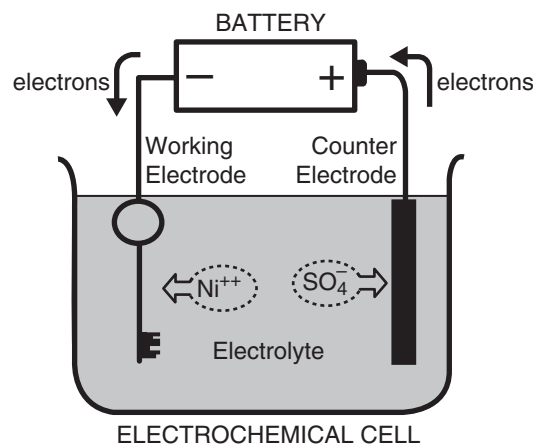


Fig. 1 Positively charged nickel ions in the electrolyte are attracted by the negatively charged key (working electrode). At the surface of the key they are reduced by gaining two electrons, and metal is deposited.

discovered that potassium cyanide was a suitable electrolyte for gold and silver electroplating. This discovery made electrodeposition an important commercial process for covering the surface of various kinds of metallic object with thin coatings of metals for corrosion protection and decorative purposes. Subsequently, baths for the deposition of other metals and alloys such as nickel, zinc, tin, and brass (an alloy consisting essentially of copper and zinc in variable proportions) were developed. For the next 100 years, the main idea was to use electrodeposition for covering the surface of inexpensive materials with a thin layer of a noble metal. By the 1940s, however, electrodeposition was rediscovered by the electronics industry. The electrodeposition of gold for electronic components was a totally different kind of application of electrodeposition techniques.

Over the years, electrodeposition became a highly developed process. Direct current (DC) power supplies were developed; anodic and cathodic reactions were described; new safer baths based on acid electrolytes, avoiding the earlier poisonous cyanide-based ones were discovered; models for the deposition process incorporating mass transport to the electrodes, charge transfer kinetics, and nucleation and growth at the working electrode were developed; and regulatory rules for waste water emission and waste disposal were created. Simultaneously, a gradual improvement in electrodeposition for large scale manufacturing processes took place.

ELECTRODEPOSITION APPARATUS AND CONCEPTS

Electrodeposition on the industrial scale requires an electrochemical cell and a DC current power supply.

This approach is relatively simple and inexpensive, and is known as galvanostatic plating system, because the current between the electrodes is controlled (maintained constant). Another important deposition mode is the potentiostatic one. This mode is a consequence of the development of electrochemical science, where electrochemical reactions at the surfaces of electrodes are carefully investigated. The electrochemist developed reference electrodes, in order to measure the potential drop near the surface of electrodes. Assuming that the electrolyte contains sufficient ions (has sufficiently high conductivity) to avoid any ohmic voltage drop, because of the resistance of the electrolyte between the electrodes, all the voltage applied by the battery (in Fig. 1) will appear near the surface of the electrodes, where a charged region is formed (usually named the double layer). It is very important to measure the voltage drop across these charged regions, because it controls the driving force for phase transformation from ion to reduced state. A simple metal foil could be used as a reference electrode; however, because of the need to have a standard electrode to measure potential drops at the surface of different types of working electrode in contact with different electrolytes, a hydrogen electrode was elected, and now all electrode potentials are quoted relative to this arbitrarily chosen reference electrode. What is always measured is the potential difference between two electrodes. By defining the potential of the hydrogen electrode as zero, it is possible to generate a table of all the possible redox reaction potentials relative to this electrode, and these potentials are called standard potentials. The standard hydrogen electrode (SHE), which is usually constructed by bubbling hydrogen gas over an immersed platinum foil, has its operation based on the redox reaction $\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$. Other reference electrodes that are robust, stable, and easily constructed than the SHE are frequently used in the laboratory, give potential measurements that can be converted to standard potentials by adding or subtracting a constant value. The most common are the calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) and silver/silver chloride electrode (Ag/AgCl).

The potential of an electrochemical cell, also known as the cell potential or electromotive force (emf) is the sum of the potential drops at the cathode and anode, where the reduction and oxidation reactions occur. With the introduction of a reference electrode the potentials of these two electrodes can be measured independently, allowing the independent investigation of the reactions that are taking place at each electrode (working or counter). These redox reactions are called half-cell reactions or simply half-reactions. The half-reaction potential E^0 can be measured with a SHE electrode at standard conditions, i.e., at electrolyte concentrations of 1 M, gas pressures of 1 atm., and

Table 1 Standard electrode potentials in aqueous solution at 25°C

Cathode half-reaction	E ⁰ (V)
Na ⁺ (aq) + e ⁻ → Na (s)	-2.71
2H ₂ O (l) + 2e ⁻ → H ₂ (g) + 2OH ⁻ (aq)	-0.83
Fe ²⁺ (aq) + 2e ⁻ → Fe (s)	-0.41
Ni ²⁺ (aq) + 2e ⁻ → Ni (s)	-0.23
2H ⁺ (aq) + 2e ⁻ → H ₂ (g)	0.00
2Cu ²⁺ (aq) + 2e ⁻ + 2OH ⁻ → Cu ₂ O (s) + H ₂ O (l)	0.17
Cu ²⁺ (aq) + 2e ⁻ → Cu (s)	0.34
O ₂ (g) + 4H ⁺ (aq) + 4e ⁻ → 2H ₂ O (l)	1.23
S ₂ O ₈ ²⁻ (aq) + 2e ⁻ → 2SO ₄ ²⁻ (aq)	2.01

Note: aq., g and l denote aqueous, gas and liquid respectively.

temperature of 25°C, and tabulated. Table 1 shows a set of standard potentials for cathode half-reactions.

The introduction of the reference electrode led to a different experimental setup for electrochemical and electrodeposition experiments. Fig. 2(A) shows an electrochemical cell with three electrodes (working-, reference-, and counter-electrodes) and a potentiostat. The potentiostat is an electronic apparatus that maintains the potential difference between the working- and reference electrodes by controlling the potential difference between the working- and counter-electrodes. Fig. 2(B) shows a block diagram of the electronic circuitry of a potentiostat with an operational amplifier that keeps the voltage between reference electrode (RE) and working electrode (W) equal to the applied voltage E at the positive terminal, by regulating the cell potential between W and counter-electrode (CE). By convention W is connected to ground.

The three-electrode cell and the potentiostat enable the potentiostatic mode of deposition mentioned above. The potentiostatic mode means that the potential of the working electrode is kept constant during

the experiment or deposition process, as depicted in Fig. 3A. An additional mode called pulsed deposition is also illustrated in Fig. 3B. In this mode, for pulsed potential, the potentiostat switches the working electrode potential between two values in order to have the potential varying as a square wave. For pulsed current deposition, a current source with a square wave output is sufficient.

The three-electrode cell and potentiostat is also a powerful experimental tool for electrochemical investigations, permitting the implementation of different techniques, such as voltammetry. This technique consists of applying a potential ramp to the working electrode, which is achieved by applying a potential ramp to the positive terminal of the operational amplifier [of Fig. 2(B)], and measuring the resultant cell current. When the applied potential starts at a defined level and comes back to the same value after a period of time, the technique is called cyclic voltammetry. When the applied potential starts at a level 1 and goes to a level 2, the resulting plot of the current versus the potential, is called a polarization curve or

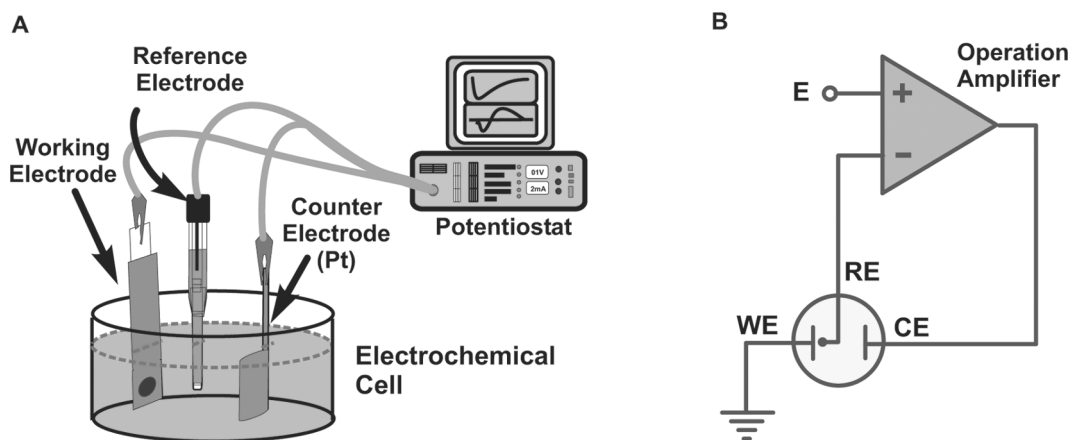


Fig. 2 (A) Electrochemical cell with three electrodes connected to a potentiostat. (B) Electronic sketch illustrating the mode of operation of a typical potentiostat.

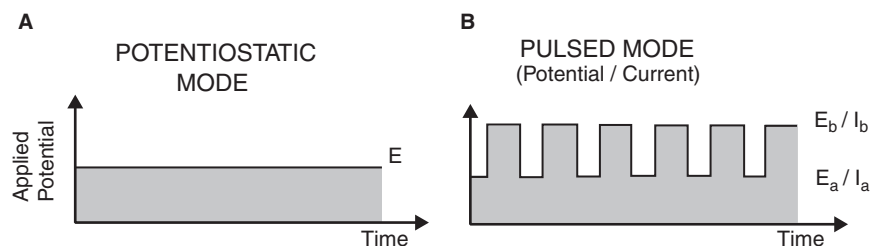


Fig. 3 Illustration of the potential as a function of time for potentiostatic and pulsed deposition modes. AQ1/PR

simply voltammogram. Fig. 4(A) illustrates a potential ramp applied to the working electrode, and Fig. 4(B) the corresponding plot for the variation of the cathodic current as a function of the cathodic potential. This figure shows a typical polarization curve for the reduction of a metal at a conductive electrode. The onset of current, indicated by an arrow, corresponds to the minimum cathodic potential at which the reaction occurs (a fundamental value for electrodeposition purposes), the peak corresponds to the maximum current at a given rate of change of potential (also known as the reduction peak), while the third characteristic feature of the plot is the saturation of the current at more negative potentials. The intensity of the reduction peak depends on the potential scan-rate, this peak being not observed, in many cases, because of other reactions that occur simultaneously.

Potentiostatic Deposition

This section will describe the potentiostatic mode using an electrolyte containing cobalt sulfate. By applying a potential ramp it is possible to obtain the polarization curve shown in Fig. 5(A). In this figure the onset of Co reduction is about -0.8 V. By selecting a deposition potential negative than this value, it is possible to obtain a deposit. Fig. 5(B) illustrates a Co

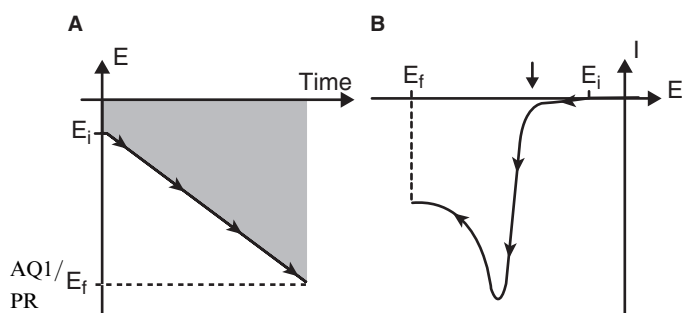


Fig. 4 Illustration of the applied potential ramp (A) to obtain a typical polarization curve (voltammogram) of metal deposition on a metal working electrode. AQ1/PR

deposit that is very homogeneous, apart from a microscopic defect because of a hydrogen bubble, obtained at a deposition potential of -1.1 V. Fig. 5(C) shows a plot of the deposition current. This plot, known as a current transient, gives information about the deposition process and allows the calculation of the electrodeposited charge from the area below the curve.

ELECTRODEPOSITION MECHANISMS

Electrodeposited Charge

Because the electrodeposition process involves the transfer of electrons to an electrode, by measuring the current in the electrochemical cell, it is in principle possible to calculate the amount of material deposited. If no other reaction occurs in parallel, then we can assume that the reaction at the working electrode in aqueous electrolyte is just the simple reduction of a metal (M)



where a metal ion M^{n+} is reduced to a metal atom M^0 after gaining n electrons. By assuming that all the metal ions reduced at the surface of the working electrode stick to this surface, the total amount of electrodeposited material can easily be calculated from the charge Q (in coulombs), which represents the product of the total amount of electrodeposited atoms N times the charge of n electrons, as given by the expression

$$Q = Nne, \quad (2)$$

where e is the charge of one electron, equal to -1.6×10^{-19} C. The charge Q is calculated from the current transient. If the deposition current is constant, Q can be calculated by simply multiplying the current I by the deposition time t ,

$$Q = It. \quad (3)$$

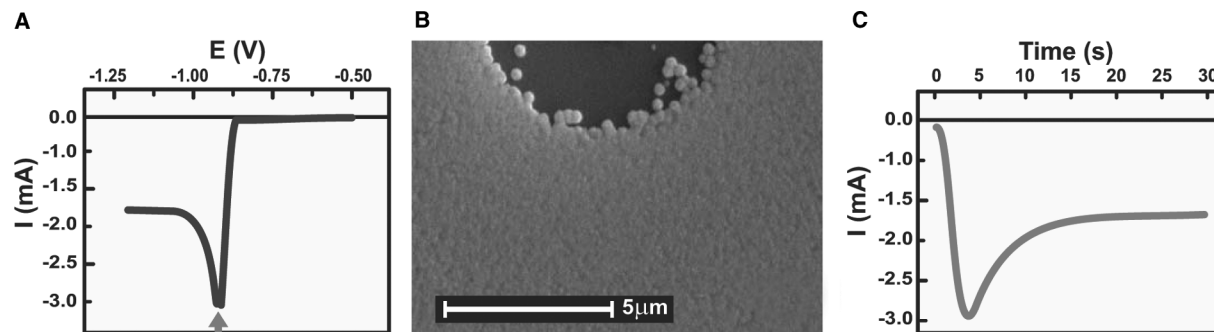


Fig. 5 (A) Polarization curve of an electrolyte containing cobalt sulfate, (B) scanning electron microscope (SEM) image of a Co deposit obtained at -1.1 V, and (C) the corresponding deposition current as a function of time (current transient). The reference electrode was saturated calomel and the working electrode semiconducting silicon. (From Ref.^[1])

However, if the current is varying during the deposition, as shown in Fig. 5(C), Q can be calculated by integrating the current $I = I(t)$ as a function of time,

$$Q = \int I(t) dt. \quad (4)$$

In order to calculate the thickness h (m) of the deposit on a known area A (m^2) of the surface of the electrode where deposition occurred, the quantity N can be expressed as

$$N = \frac{mN_a}{M}, \quad (5)$$

where m is the electrodeposited mass (g), N_a is Avogadro's number (the number of atoms in a mole, equal to 6.02×10^{23}) and M is the atomic weight. Using the density d (g/m^3), given by $d = m/V$, where the volume V (m^3) is given by the product of the area, and the thickness, $V = Ah$, Eq. (5) can be rewritten as

$$N = \frac{dAhN_a}{M}, \quad (6)$$

and Eq. (2) rewritten as

$$Q = \frac{ndAhN_a e}{M} = \frac{ndAhF}{M} \quad (7)$$

where F is Faraday's constant, defined as $F = N_a e$, equal to 96,485.34 C. By rearranging Eq. (7) and knowing the quantities M , Q , n , d , A and F , the thickness can be easily calculated from:

$$h = \frac{MQ}{ndAF}. \quad (8)$$

This calculation gives a deposit thickness in meters that has to be converted into more adequate units as microns ($1 \mu m = 10^{-6} m$) or nanometers ($1 nm = 10^{-9} m$). For a precise calculation of the thickness of deposits, it is necessary to take into account possible electrode reactions that occur simultaneously with the main reaction. One very common example is the hydrogen evolution reaction, $2H^+ + 2e^- \rightarrow H_2$. This reaction is so rapid, in conditions such as relatively high cathodic potentials in acidic electrolytes, that it dominates the exchange of electrons at the surface of the electrode. The contribution of hydrogen evolution to the cathodic current must be determined in order to obtain the efficiency of the plating process. This may be done indirectly by measuring the thickness of the deposit and calculating the amount of charge corresponding to "missing" metal. The presence of hydrogen during the deposition has several effects on the metallurgical properties of the deposits. One of these effects is the formation of gas bubbles that mask the surface of the electrode locally, introducing microscopic defects in the electrodeposited layers [see example of this effect in Fig. 5(B)].

Mass Transport

Electrodeposition has the ability to produce a relatively uniform distribution of metal upon a cathode of irregular shape. Though the uniformity depends on the distribution of electric fields inside the electrolyte toward the surface of the electrode, other important factors have to be considered. The addition of agents (additives) to the electrolyte, for example, can affect the microscopic mechanism of electrodeposition, reducing the roughness of the deposit and producing a visual effect known as brightening.

In order to obtain layers with a desired property, such as uniform thickness and low roughness, or an

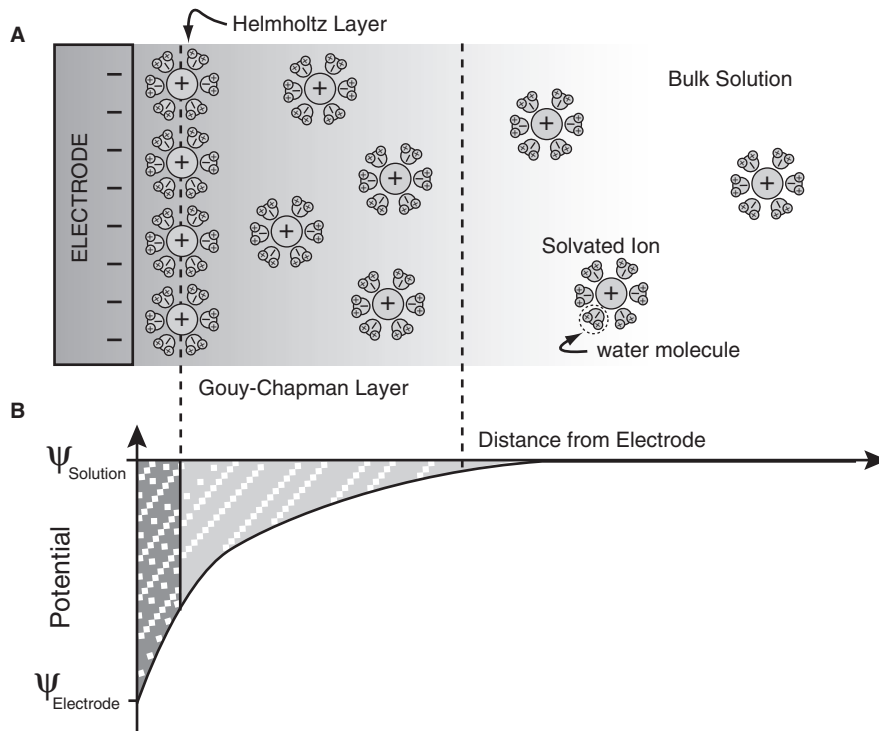


Fig. 6 Illustration of the electric double layer (A) and potential drop (B) near the surface of the electrode. AQ1/PR

electrolyte with high filling capacity, i.e., with the ability to produce deposits inside holes or lithographic features, one has to consider carefully the transport of different species inside the electrolyte and the reaction rates of these species on the surface of the electrode.

Basically, three mechanisms are responsible for mass transport inside an electrochemical cell: diffusion, migration, and convection. Diffusion is mass transport because of concentration gradients, i.e., variations in the concentration of a species with position. Diffusion occurs mainly near the electrode surface because of gradients created by the consumption of species that undergo redox reactions and are incorporated into the deposit. This incorporation process depletes the deposition species near the electrode, generating the concentration gradient.

The simple introduction of an electrode into an electrolyte will lead to an exchange of charge between

electrolyte and electrode. An electric double layer, illustrated in Fig. 6, will be formed. Fig. 6(A) shows the double layer in greater detail. When the exchange process reaches equilibrium the double layer thickness depends on the physical and chemical properties of the electrode/electrolyte interface. In general, the description of the double layer considers the existence of two regions named the Helmholtz layer, a monolayer of ions on the surface of the electrode, and the Gouy-Chapman layer, a region that penetrates the bulk of the electrolyte with decreasing charge and concentration gradients. In the figure, the ions are shown with a sheath of water molecules. This solvation sheath is because of the electrostatic attraction of polar water molecules and the ionic species. Fig. 6(B) illustrates the potential drop near the surface of the electrode because of the presence of the double layer. In the bulk of the electrolyte the potential drop is

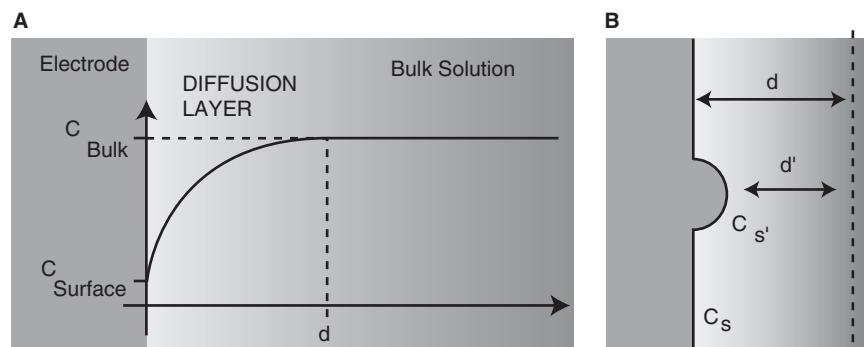


Fig. 7 (A) Idealized profile of the concentration gradient near the surface of the electrode and (B) an illustration of a deposition instability in the presence of an asperity. AQ1/PR

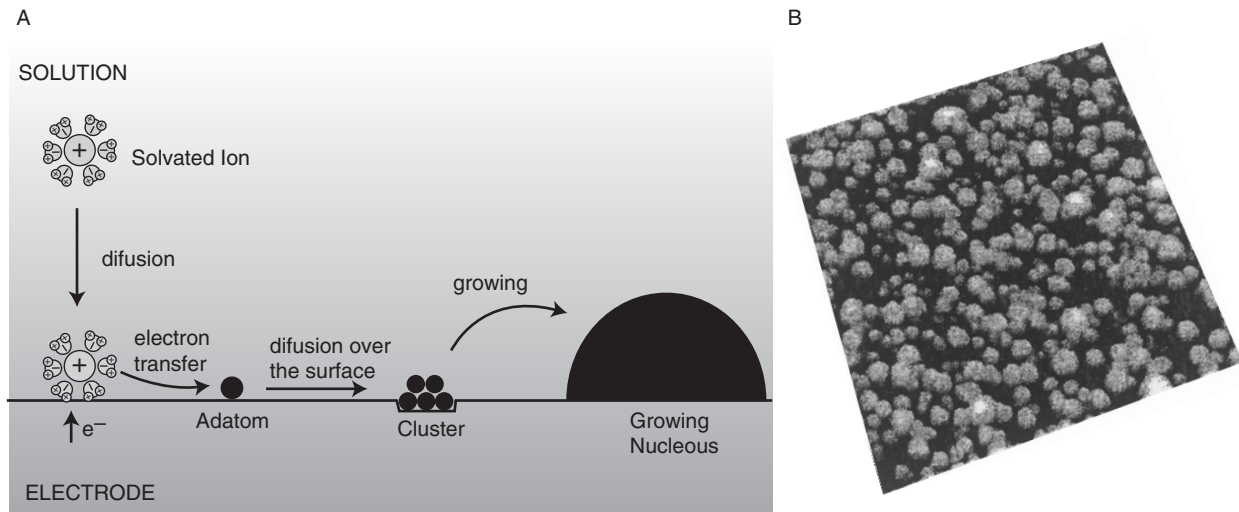


Fig. 8 (A) Mechanism of formation of electrodeposits on the surface of an electrolyte and (B) an atomic force microscope (AFM) image reveals the granular nature of a Co deposit. (From Ref.^[1])

normally very low, because this region is not depleted of ionic species.

Beyond the double layer, there is a depleted region named the diffusion layer with a thickness of microns, much wider than the double layer, formed during deposition by the consumption of a particular species. Fig. 7(A) is a plot of the concentration of an ionic species as a function of the distance from the surface of the electrode, showing the diffusion layer. The consumption of ions because of metal deposition generates a concentration gradient that, in steady-state conditions, is essentially determined by the redox reaction rate. If the consumption of ions arriving at the surface by diffusion is very high, the concentration of ions at the surface C_s is effectively zero, and the deposition process is controlled by diffusion. If the consumption is low, then the ion concentration at the surface is different from zero and the deposition is controlled by kinetics, i.e., by the velocity of the reaction.

Electrodeposition in the diffusion-limited regime is very sensitive to asperities on the surface of the

electrode, as shown in Fig. 7(B). These morphological structures reduce the size of the diffusion layer, thereby increasing the concentration gradient and hence the current. The local increase in current increases the deposition rate, favoring further growth of the asperities, and consequently an increase in roughness of the whole electrodeposited layer. This effect is known as deposition instability.

Inside the bulk of the electrolyte, mass transport is mainly because of migration, a mechanism of ionic motion caused by the presence of an applied electric field. In the electrochemical cell the potential drop creates an electric field that is much more intense in the regions near the surface of the electrodes, but is sufficiently intense in the bulk of the electrolyte to promote the migration of the ions to the border of the diffusion layers.

The third important mechanism of mass transport is convection. In this case, the fluid flows in an uncontrolled manner because of natural density gradients (gradients caused by concentration and temperature

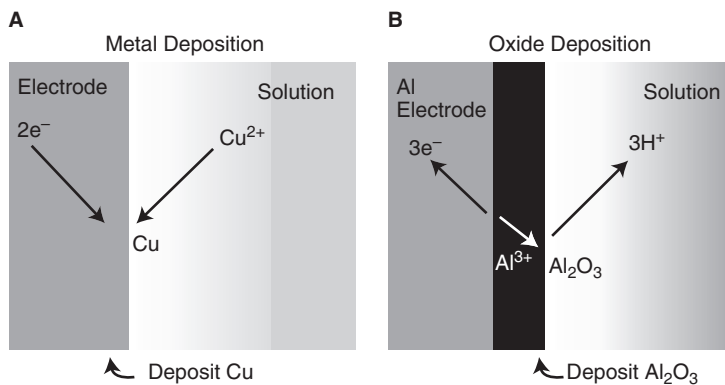


Fig. 9 Electrode reaction for (A) the cathodic electrodeposition of Cu and (B) the anodic electrodeposition of Al oxide.

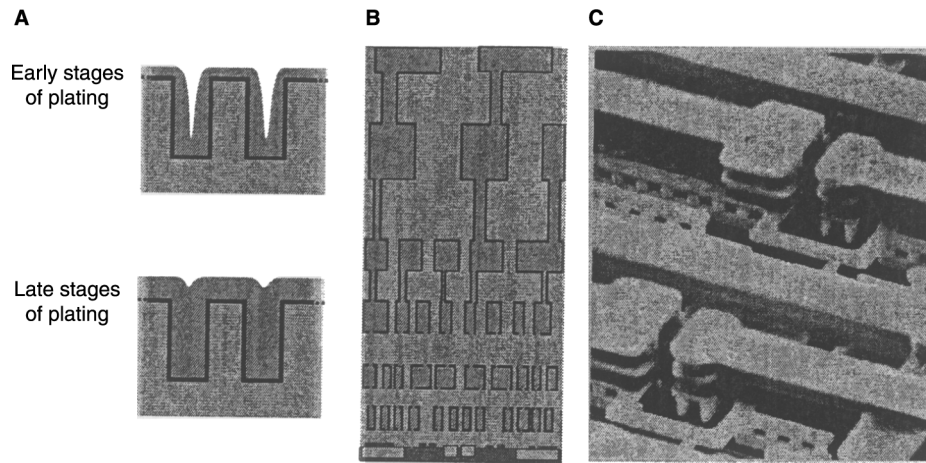


Fig. 10 (A) Sequence of filling of a trench profile for the fabrication of Cu interconnects, (B) a cross-section illustration of a six-level wiring structure, and (C) SEM view of IBM's first-to-market six level copper interconnect technology. (From Ref.^[2].)

fluctuations). Convection can also be produced in a controlled manner by different methods, such as mechanically stirring the electrolyte.

Growth Mechanisms

To complete the explanation about the mechanisms of electrodeposition, it is very important to give an idea about the formation of the deposits. A model for the electrodeposition process considers a solvated ion going through the diffusion layer as a first step, loosening of the solvation sheath by transferring electrons with electrode and being adsorbed (adatom) as the second step, and surface diffusion and incorporation in an energetically favorable site as the third step. The deposition sites can be punctual or extended surface defects, such as vacancies or kinks, known in general as nucleation sites. The nucleation sites allow the formation of nuclei (islands) that evolve to grains, forming compact deposits that grow on top of the surface of the electrode. Fig. 8(A) depicts the mechanism of layer growth and Fig. 8(B) shows an atomic force

microscopy (AFM) image of an electrodeposited layer from an electrolyte containing cobalt sulfate. The image clearly reveals the formation of Co grains on top of electrode surface.

Electrode Reactions

The current that flows at the working electrode may be divided into two kinds: faradaic and non-faradaic. The faradaic processes are the ones where charges are transferred across the liquid–solid interface. These processes are called faradaic because they follow Faraday's law, which says the amount of substance that undergoes oxidation or reduction at each electrode is directly proportional to the amount of electricity that passes through the cell. Two faradaic processes that are directly related to electrodeposition are shown in Fig. 9, where Fig. 9(A) represents simply the deposition of Cu by reduction of Cu^{2+} and Fig. 9(B) the growth of Al anodic oxide by oxidation of metallic aluminum, this being an example of anodic electrodeposition. Non-faradaic processes are struc-

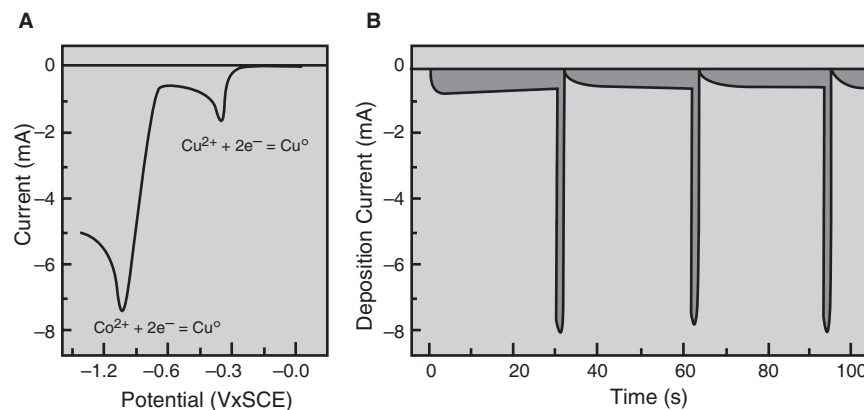


Fig. 11 (A) Voltammogram of an electrolyte containing two salts, Co and Cu sulfates and (B) pulses corresponding to the alternate deposition of a Cu/Co multilayer. The electrode is semiconducting Si. (Courtesy of L. Seligman, Universidade Federal de Santa Catarina).

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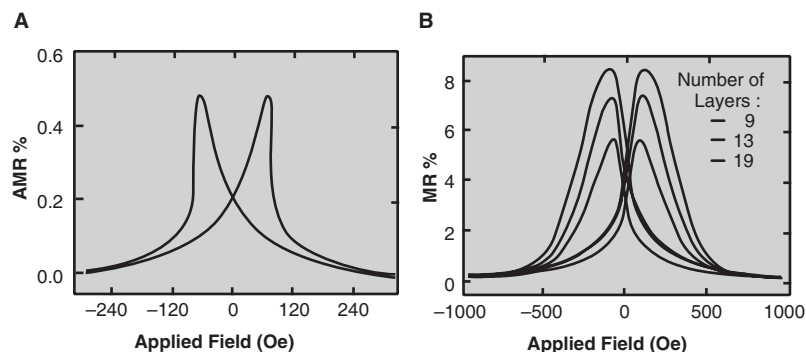


Fig. 12 (A) AMR of single layer of Co¹¹ and (B) GMR results depending on the number of layers. (From Ref.^[5].) The substrate is semi-conducting Si. AQ1/PR

tural changes of the electrode–solution interface, such as absorption and desorption of species that change the potential of the electrode and solution composition without charge transfer.

ELECTRODEPOSITION IN MICROELECTRONICS

Recently, there has been a boom in the use of electrodeposition for microelectronics. The microelectronics industry came to the conclusion that the electrodeposition of Cu is the ideal manufacturing process for wiring for semiconductor logic and memory devices. Wiring is the network of wires that interconnects the devices (transistors) on integrated-circuit chips. Copper is a highly conductive metal and is relatively easy to electrodeposit. Since 1997, Cu has been successfully used for the production of interconnects.^[2] Nowadays, such interconnects are electrodeposited in trenches with widths of 0.13 μm or less. The ability to fill trenches and vias with a plated material is called superfilling and is illustrated in Fig. 10(A). The cross-section of the device illustrated in Fig. 10(B) depicts the multilevel wiring structure of an integrated circuit and Fig. 10(C) shows a real arrangement of electrodeposited interconnects in a device fabricated by IBM.

ELECTRODEPOSITION IN NANOSCIENCE AND NANOTECHNOLOGY

Simultaneously, with the rapid growth of electrodeposition in microelectronics, a new trend based on the electrodeposition of materials, structures, particles, devices, etc., generally called nano-objects, with dimensions below 100 nm commenced. Nano-objects are fundamental for nanoscience investigations and nanotechnology development. A nano-object is of particular interest if it has physical properties that differ from objects that have macroscopic sizes. Quantization of energy, for example, is observed in systems with greatly reduced size, such as atoms, molecules, and nanostructures.

Electrodeposition is an elegant and efficient technique for the production of nano-objects. Using the pulse deposition mode, it is possible to control the amount of atoms to be deposited with great precision. That is, pulsing with pulse durations of a few milliseconds to a few seconds, allows the deposition of clusters of atoms or layers with thickness of a few to hundreds of nanometers.

A typical example of an electrodeposited nanostructure is a multilayered structure. By having two salts in the electrolyte and applying two potentials in alternation, it is possible to deposit multilayer structures,

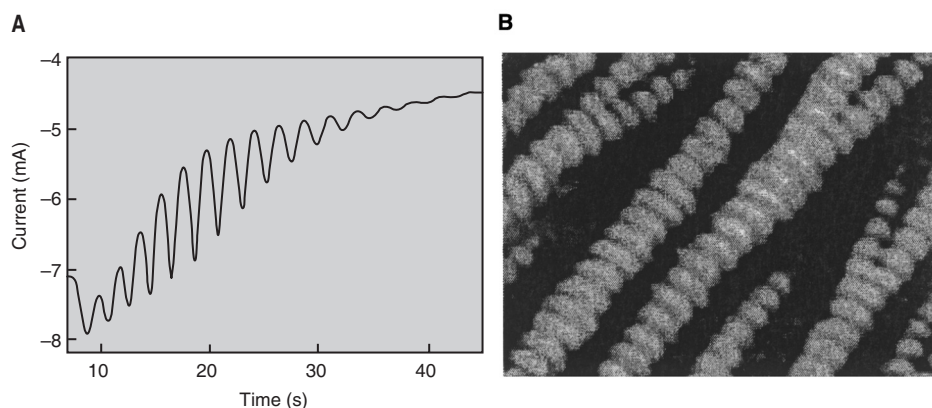


Fig. 13 (A) Spontaneous current oscillations during deposition at constant applied potential using an electrolyte containing Cu sulfate and lactic acid (Courtesy of R.G. Delatorre, Universidade Federal de Santa Catarina) and (B) SEM image of Cu/Cu₂O multilayered wires. (From Ref.^[8].) AQ1/PR

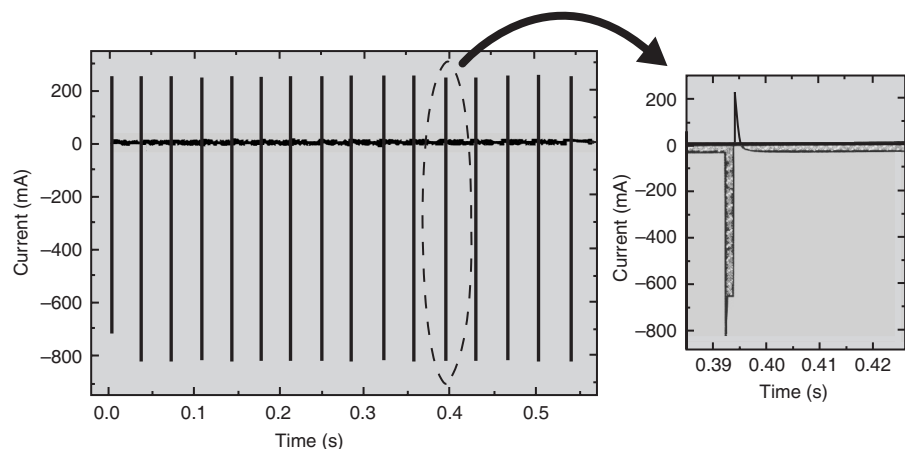


Fig. 14 Sequence of ultrafast pulses for the deposition of a nanostructured $\text{Cu}_{48}\text{Ni}_{52}$ alloy. (From Ref.^[10])

which are artificially fabricated materials that have application in the electronics industry. Fig. 11(A) shows the polarization curve for an electrolyte containing two salts, CuSO_4 and CoSO_4 , where the reduction peaks of each metal are clearly seen. Pulsing the cathodic potential rapidly between a value at which only Cu is reduced, and one at which a Co-rich alloy is reduced, generates a deposit that is a Cu/Co multilayer with individual layers of nanometric thickness. The layer thickness may be controlled by integrating the current in real time and calculating the electrodeposited charge or, more simply, by controlling the deposition time. Fig. 11(B) shows typical current transients with characteristic peaks for each layer electrodeposited. The Co deposition current is much higher than the Cu one because to assure the deposition of a Co-rich alloy the concentration of Co sulfate in the electrolyte has to be much higher than the Cu sulfate concentration.

A multilayer structure with one of the repeating layers being a magnetic material is called magnetic

multilayer. If the individual layers are only a few nanometers thick, which is easily achievable by electrodeposition, the electric resistance will vary with the magnetic field, an effect discovered very recently and known as giant-magnetoresistance (GMR).^[3,4] The first observation of a magnetoresistive effect was by Lord Kelvin in 1857 by measuring the electrical resistance of magnetic alloys. Nowadays, the effect that he observed is called anisotropic magnetoresistance (AMR), and its magnitude does not exceed 6%. The GMR effect is about one order of magnitude greater than AMR and depends on many factors, such as the thickness and number of individual layers, the magnetic material used and the preparation method, and is observed also in non-layered granular structures. Magnetoresistive materials have been intensively used in the high-technology industry as magnetic sensors and reading heads for computer hard disk drives. Fig. 12(A) shows the magnetoresistance of a single layer of electrodeposited Co, similar to the one

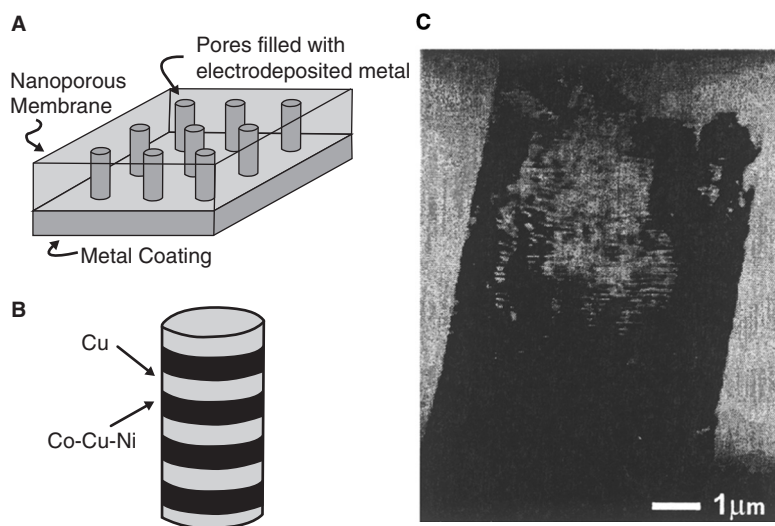


Fig. 15 (A) Alumina membrane with nanopores, (B) schematic view of a layered nanowire, and (C) TEM image revealing the layered structure of a Cu/CuCoNi nanowire grown in alumina nanopores. (From Ref.^[11])

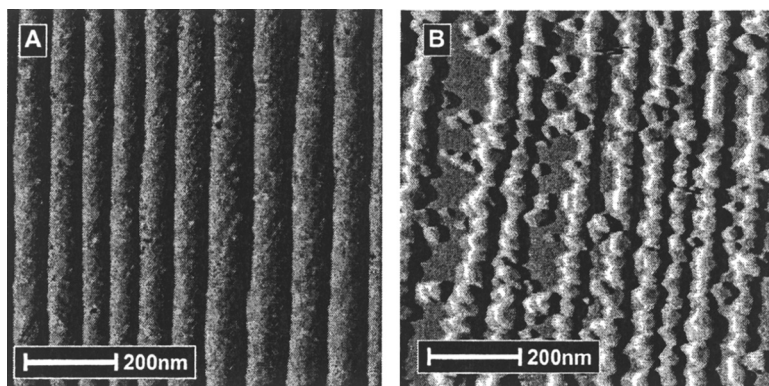


Fig. 16 (A) High-resolution AFM image of an atomically flat single crystal of Si showing large terraces and parallel steps and (B) nanowires of Au electrodeposited preferentially at the step edges. (From Ref.^[12])

depicted in Fig. 5, which shows an AMR effect of 0.5%. Fig. 12(B) illustrates the case of a magnetic multilayer, also electrodeposited, with the effect depending on the number of layers, reaching in this case a maximum of 8.5% for 15 Co/Cu layers.

An interesting achievement of electrodeposition in the preparation of nanostructures is the self-assembly of multilayers.^[6] An electrolyte containing copper sulfate (CuSO₄) and lactic acid (C₃H₆O₃) is a standard example because under certain experimental conditions the cell current oscillates spontaneously leading to the growth of a nanometric Cu/Cu₂O multilayer. In Fig. 13(A) the spontaneous oscillations of the deposition current are illustrated, though a natural damping of the magnitude is observed. However, in stirred solutions the oscillatory behavior can be maintained for several days.^[7] Fig. 13(B) shows a SEM image of filaments of spontaneously grown Cu/Cu₂O multilayers.^[8]

The explanation for the spontaneous formation of multilayers lies in variations in the pH.^[6,7,9] In the growth process, the electrodeposition of Cu₂O is favored, as it has an equilibrium potential more positive than that of Cu deposition (Table 1). However, the reaction $2\text{Cu}^{2+} + 2\text{e}^{-} + 2\text{OH}^{-} \leftrightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$ depletes the OH⁻ species near the electrode, locally decreasing the pH and favoring the deposition of Cu. The above process is repeated, because the OH⁻ concentration is re-established during Cu²⁺ reduction.

Additionally, by having an experimental setup with a high-speed data acquisition system, it is possible to control deposition pulses with durations below milliseconds. This ultrafast pulsing method was called precision electrodeposition and allowed the deposition of sub-monolayer quantities of material.^[10] Precision electrodeposition was demonstrated for the CuNi system, as shown in Fig. 14, where a sequence of ultrafast current pulses for the electrodeposition of a nanostructured CuNi alloy with a controlled composition of 48% Cu and 52% Ni is displayed. The duration of the pulses (tens of milliseconds), allows the deposition

per cycle of 0.25 monolayer of Cu and 0.25 monolayer of Ni.

Nanowires

A special characteristic of electrodeposition is the fact the deposition occurs only where there is an electrical connection to the external circuit. This is a great advantage because it allows the deposition to be area selective. By covering the electrode surface with a patterned insulating layer, electrodeposition will occur only on the exposed areas. This makes electrodeposition an ideal method for growing materials on previously determined patterns and also for filling high-aspect ratio templates.

This advantage can be used for growing nanowires (wires with nanometric diameter). Nanoporous membranes that can be fabricated by the anodic oxidation of aluminum are appropriate templates. This process leads to the formation of an alumina layer with parallel nanopores, as shown in Fig. 15(A), which can then be filled by electrodeposition. Fig. 15(B) shows a schematic view of a multilayer nanowire and Fig. 15(C) a transmission electron microscopy image of a Cu/CuCoNi layered nanowire grown in the nanopores.

A different way to electrodeposit nanowires is by using the surface of a single crystal as a template. Fig. 16(A) shows an AFM image of a silicon surface, revealing large terraces with parallel steps. By electrodepositing Au at relatively low deposition rates, the steps act as deposition sites favoring the formation of wires of nanometric size along their edges, as shown in Fig. 16(B).

CONCLUSIONS

Electrodeposition is a process widely used in industry. In this entry, emphasis was given to fundamental

1 aspects and to future potential applications of this
2 technique.

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6
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