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Review Article

Electrodeposition for nanoprecision manufacturing of integrated circuits: A new paradigm from molecular design to multiscale modeling

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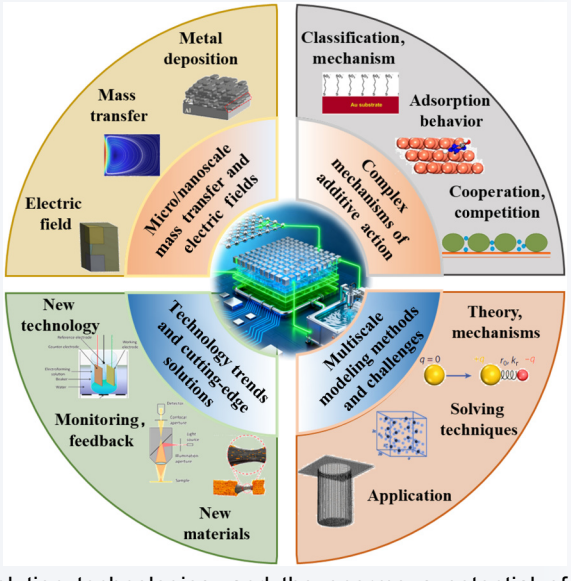
ABSTRACT: The continuous advancement of integrated circuit (IC) manufacturing technology has posed unprecedented challenges to the electronic electroplating process, with its core lying in achieving precise regulation of metal deposition behavior within micro/nanoscale structures, especially those with high aspect ratios (HAR). This review systematically summarizes the key progress in the research on multi-scale metal nucleation and growth mechanisms in IC electronic electroplating. We first analyze the unique mechanisms of mass transfer and electric field distribution at the micro/nanoscale, revealing the electric field inhomogeneity caused by geometric effects and polarization effects in HAR structures, as well as the diffusion-dominated mass transfer process. Furthermore, we delve into the complexity of additive effects, including their adsorption behavior in nano-confined spaces and the intricate synergistic and competitive relationships among inhibitors, accelerators, and levelers, while reviewing the development of innovative additives based on molecular design. Targeting the aforementioned complex system involving multi-physics and multi-scale coupling, this paper focuses on elaborating the construction methods of cross-scale theoretical models, the latest advances in multi-physics coupling solution technologies, and the enormous potential of machine learning (ML) and artificial intelligence (AI) in enhancing model predictive capabilities and optimizing processes. Finally, we prospect the frontier development directions such as novel electroplating processes, *in-situ* monitoring and feedback control technologies, exploration of new material systems, and process integration and equipment innovation. This review aims to provide a comprehensive theoretical framework and technical perspective for in-depth understanding of the fundamental mechanisms of micro/nano electronic electroplating and the development of next-generation high-performance interconnect technologies.



KEYWORDS: integrated circuits, electronic plating, multiscale, metal deposition

1 Introduction

Integrated circuit (IC) manufacturing technology has entered the "post-Moore era", and three-dimensional (3D) integration technologies such as through-silicon vias (TSVs) have become the key path to sustain the growth of computing power [1, 2]. Against this backdrop, electronic electroplating, as the core process for metallizing micro/nano interconnect structures, faces increasingly prominent technical bottlenecks: achieving the void-free and defect-free superconformal metal filling in micro/nano structures with an aspect ratio exceeding 10:1 [3, 4]. The root cause of this severe challenge lies in the fact that the electrodeposition at the micro/nanoscale is an extremely complex process involving the coupling of multiple physical fields (electric field, flow field, and

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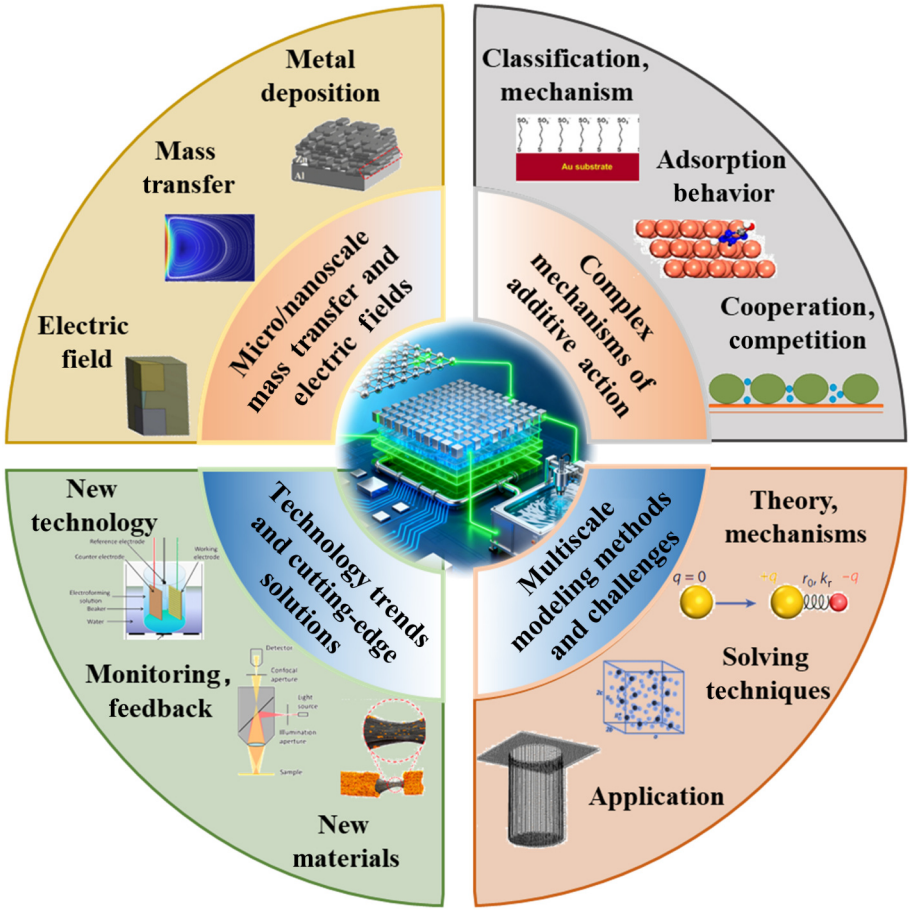
concentration field) and the interweaving of phenomena from the molecular and microscale to the macroscale [5, 6]. Traditional empirical process optimization can no longer meet the requirements, and it must be based on a profound understanding of basic scientific issues such as the laws of mass transfer and electric field distribution at the micro/nanoscale, the mechanism of additive molecule action, and cross-scale theoretical modeling methods [7, 8].

Current research exhibits a fundamental shift from macroscale experience to microscale mechanisms, from single-physics field to multi-physics field coupling, and from "trial-and-error methods" to the combination of "model-driven" and "data-driven" approaches [9–12]. The core of this transformation lies in addressing three interrelated key scientific questions: (1) Within nano-confined spaces, how do the highly inhomogeneous electric field distribution (e.g., the current density ratio between the orifice and the bottom of the hole can reach 13:1) and the diffusion-dominated mass transfer mechanism collectively affect the transport and deposition kinetics of metal ions? (2) How do additive molecules (inhibitors, accelerators, and levelers) adsorb, assemble, and interact at the solid/liquid interface? What new characteristics do their complex "synergistic–competitive" relationships exhibit at the nanoscale, and how can they be regulated through molecular design? (3) How to construct a full-chain theoretical model that can seamlessly connect electron transfer at the quantum scale to reactor engineering at the macroscale, and achieve efficient transmission and verification of information between different scales?

To systematically address the aforementioned questions, this review aims to provide a comprehensive summary and prospective analysis of the research on multi-scale metal nucleation and growth mechanisms in IC electronic electroplating (Scheme 1). First, this paper will delve into the fundamental principles of electric fields and mass transfer at the micro/nanoscale, as well as their unique behaviors in complex structures such as TSVs. Furthermore, it will focus on exploring the complexity of additive action mechanisms, including their adsorption behavior in nano-confined spaces, intermolecular interactions, and innovative design strategies based on quantum chemical calculations and machine learning. Subsequently, the latest methods for multi-scale model construction will be systematically reviewed, covering cross-scale theoretical frameworks, multi-physics coupling solution technologies, and innovative algorithms empowered by artificial intelligence. Finally, this paper will prospect the development trends of cutting-edge technologies such as pulse electroplating, *in-situ* monitoring, new material systems, and intelligent equipment. By establishing a complete knowledge framework from basic mechanisms to frontier applications, this review intends to provide researchers and engineers across fields with a clear theoretical map and technical path, collectively promoting the breakthrough and development of next-generation high-performance interconnect technologies. The "new paradigm" proposed in this review essentially represents a shift from the traditional empirical trial-and-error approach toward a systematic framework that integrates molecular design, cross-scale modeling, and artificial intelligence. It emphasizes the use of microscopic mechanistic studies, multi-physics coupled models, and data-driven intelligent algorithms to achieve accurate



Scheme 1 Micro/nano electronics electroplating: schematic diagram of the framework from multiphysics mechanisms to technological applications.

prediction and control of the electrodeposition process from the molecular to the macroscopic scale, thereby providing a new pathway for next-generation nanoscale precision manufacturing.

2 Mass transfer and electric field distribution mechanisms at the micro/nanoscale

2.1 Theory of electric field distribution in high aspect ratio micro/nanostructures

In the IC electroplating process, the electric field distribution is a key factor determining the morphology and quality of metal deposition [13, 14]. In HAR micro/nanostructures, the electric field distribution exhibits distinct characteristics from those in macroscale systems [15]. According to Laplace's equation, the electric field distribution satisfies $\nabla^2\varphi = 0$, where φ denotes the electric potential. However, in complex geometric structures, especially blind vias or through-holes with HAR, the complexity of boundary conditions leads to extremely inhomogeneous electric field distribution [16].

In a typical TSV structure, the electric field distribution is influenced by multiple factors. Firstly, the geometric effect. The current density concentration at the via opening results in an electric field intensity significantly higher than that at the via bottom [17]. Secondly, the resistance effect. As the deposition process proceeds, the increase in metal layer thickness alters the local resistance distribution, thereby affecting the electric field distribution [18]. Thirdly, the electrochemical polarization effect, including concentration polarization and electrochemical polarization, which become more prominent at the micro-nano scale [19].

Numerical simulation studies have shown that in microvias with a diameter of 5 μm and a depth of 25 μm, the ratio of current density at the via bottom to that at the via opening can reach 13:1 [20, 21]. This significant difference in current density leads to a much higher metal deposition rate at the via opening than at the bottom, easily causing the "premature closure" phenomenon, where the via opening is covered by metal before the bottom is fully filled, ultimately forming void defects inside the via [22].

2.2 Analysis of multi-scale mass transfer mechanisms

Mass transfer is another critical step in the electroplating process, involving three basic mechanisms: diffusion, electromigration, and convection [23–25]. At the micro-nano scale, the relative importance of these three mechanisms undergoes significant changes, exhibiting characteristics entirely different from those at the macro scale.

The diffusion mechanism dominates in micro-nano structures. According to Fick's second law, the diffusion flux is given by $J = -D\nabla c$, where D is the diffusion coefficient and c is the concentration. In HAR structures, because the characteristic size is much smaller than the thickness of the diffusion boundary layer, diffusion becomes the main factor limiting the mass transfer rate (Figs. 1(a) and 1(b)). Studies have shown that when the aspect ratio is greater than 1, the diffusion of nickel ions dominates the mass transfer process. For example, in microvias with dimensions of 8 μm × 4 μm, the contribution of diffusion mass transfer is approximately 2000 times higher than that of convective mass transfer; even in larger structures of 200 μm × 100 μm, diffusion is still about 400 times stronger than convection [26].

The electromigration mechanism exhibits a relatively complex role at the micro-nano scale. Under electroplating conditions, the electromigration of copper ions toward the cathode is in the same direction as diffusion, which helps improve mass transfer efficiency. However, in micro-nano structures, the role of electromigration becomes complicated due to the inhomogeneity of the electric field distribution. Through numerical simulations, Braun et al. found that at low supporting electrolyte concentrations, electromigration significantly enhances local deposition at the bottom, but its contribution is weak under high-acid conditions (Fig. 1(c)). Notably, in regions with extremely small characteristic sizes, diffusion driven by concentration gradients still dominates, and the influence of electromigration is relatively secondary [27].

The convection mechanism is severely restricted in micro-nano structures. In macroscale systems, forced convection can significantly improve mass transfer efficiency, but inside micro-nano structures, due to the extremely small characteristic size, the Reynolds number of the fluid is very low, and the flow exhibits laminar characteristics. Zhao et al. pointed out that acoustic streaming can hardly be generated inside microvias and can only improve the mass transfer of copper ions in the region near the via opening. In ultrasonic-assisted electroplating, although increasing ultrasonic power can increase the average liquid velocity inside microvias, this effect decays rapidly with increasing distance from the transducer (Figs. 1(d) and 1(e)) [28].

2.3 Differences in deposition behavior among different metal systems

In IC manufacturing, different metal systems exhibit markedly distinct deposition behaviors, primarily due to their differing physicochemical properties.

Copper electroplating is currently the most widely used technology, mainly employed for TSV filling and interconnect structure fabrication. Copper possesses excellent electrical conductivity (1.7×10^{-8} Ω·m) and thermal conductivity (401 $W \cdot m^{-1} \cdot K^{-1}$), with a mature electroplating process [29]. In microvia filling, copper electroplating typically adopts an acid copper sulfate system, incorporating organic additives such as polyethylene glycol (PEG), bis(3-sulfopropyl) disulfide (SPS), and chloride ions to achieve a "bottom-up" superconformal filling effect (Fig. 2(a)) [30]. The electrodeposition process of copper involves a two-step reduction reaction from Cu^{2+} to Cu, and the formation and diffusion of the intermediate product Cu^{+} exert a significant influence on the deposition quality [11, 31].

Although copper dominates in most high-performance applications, aluminum electroplating still exhibits certain advantages in low-temperature processes and special application scenarios. Aluminum has a relatively low melting point (660 °C) and a low density (2.7 $g \cdot cm^{-3}$), and can form a natural passivation layer in air [32]. However, aluminum has a relatively negative standard electrode potential (−1.66 V vs. standard hydrogen electrode (SHE)) and is prone to the hydrogen evolution reaction (HER) in aqueous electrolytes, which severely limits its Coulombic efficiency. To address this issue, researchers typically adopt ionic liquids or urea-aluminum chloride-based non-aqueous electrolyte systems to suppress side reactions and achieve reversible aluminum deposition. In the research on aluminum-air batteries, Liu et al. pointed out that by adjusting the length of non-polar groups in quaternary ammonium salts, a "physicochemical hydrophobic interface" can be constructed, which effectively inhibits HER and improves battery capacity and cycling stability (Fig. 2(b)) [33].

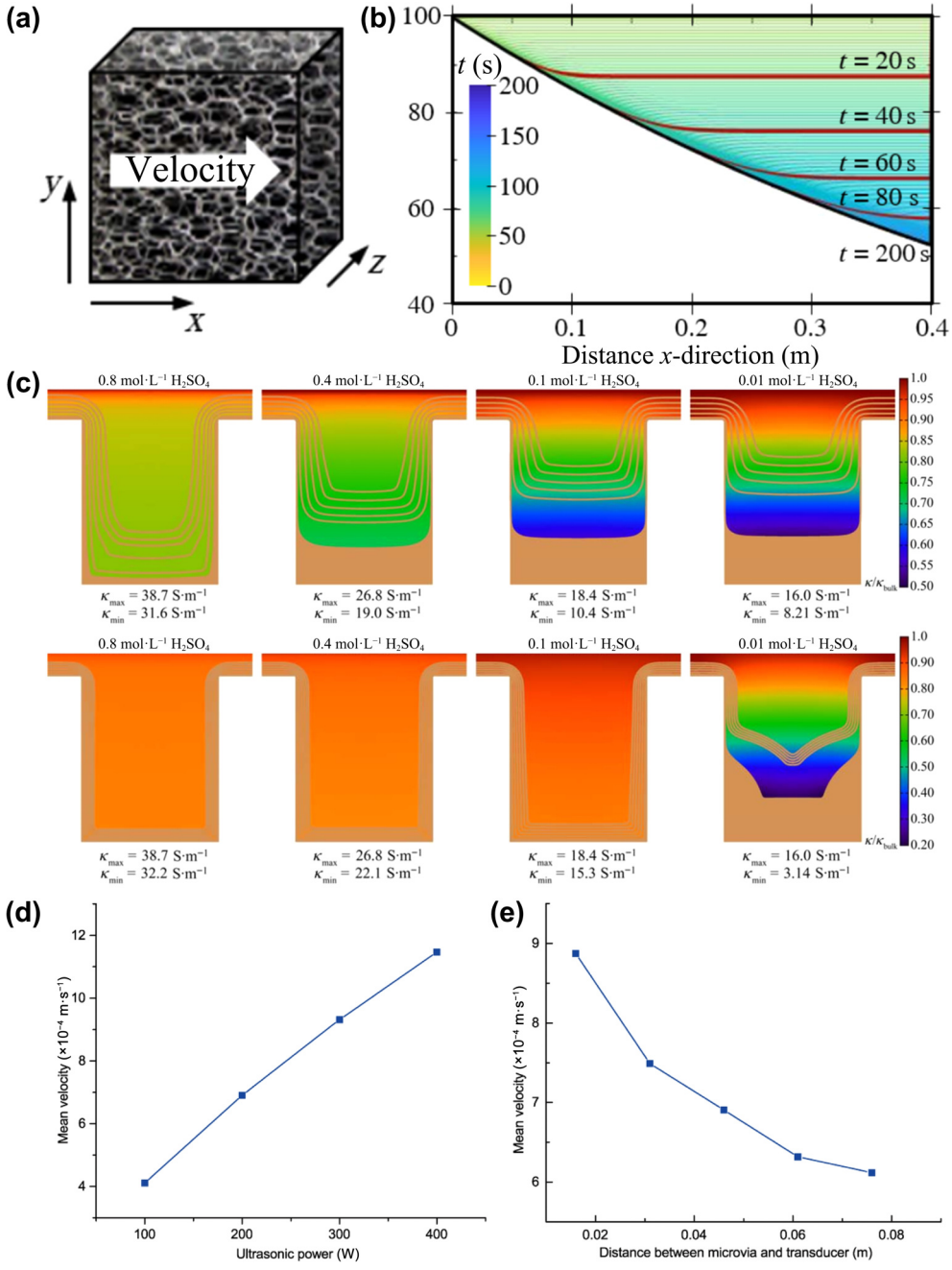


Figure 1 (a) Direction of velocity in *x*-direction. (b) Concentration distribution during the electrodeposition process for each time step over *x*-direction. (c) Simulations of galvanostatic copper electrodeposition after 30 min in microvias with a boundary layer thickness of 10 μm at the indicated sulfuric acid concentrations. Reproduced with permission from Ref. [27], © Braun, T. M. et al. 2022. (d) Mean velocities inside microvias with different ultrasonic powers. (e) Mean velocities inside microvias with different distances between the microvias and transducer. Reproduced with permission from Ref. [28], © Elsevier B.V. 2018.

In semiconductor processes requiring high temperature and high reliability, tungsten chemical vapor deposition (CVD) is irreplaceable in certain critical applications, particularly in contact hole and via filling [34]. Tungsten possesses an extremely high melting point (3422 °C), excellent electromigration resistance, and good step coverage capability. However, the tungsten CVD process requires a high temperature (> 400 °C) and involves toxic WF_6 gas, which increases process complexity and cost. In a review, Goyal et al. pointed out that although emerging materials such as carbon nanotubes (CNTs) have shown potential in HAR TSVs, tungsten is still widely used in polysilicon dielectric filling and local interconnects due to its thermal stability and process maturity (Fig. 2(c)) [1].

2.4 Numerical simulation methods and experimental validation techniques

To gain a deeper understanding of mass transfer and electric field distribution mechanisms at the micro- and nano-scales, researchers developed various advanced numerical simulation methods and experimental validation techniques [35–37].

In terms of numerical simulation, the arbitrary Lagrangian–Eulerian (ALE) method has become a mainstream

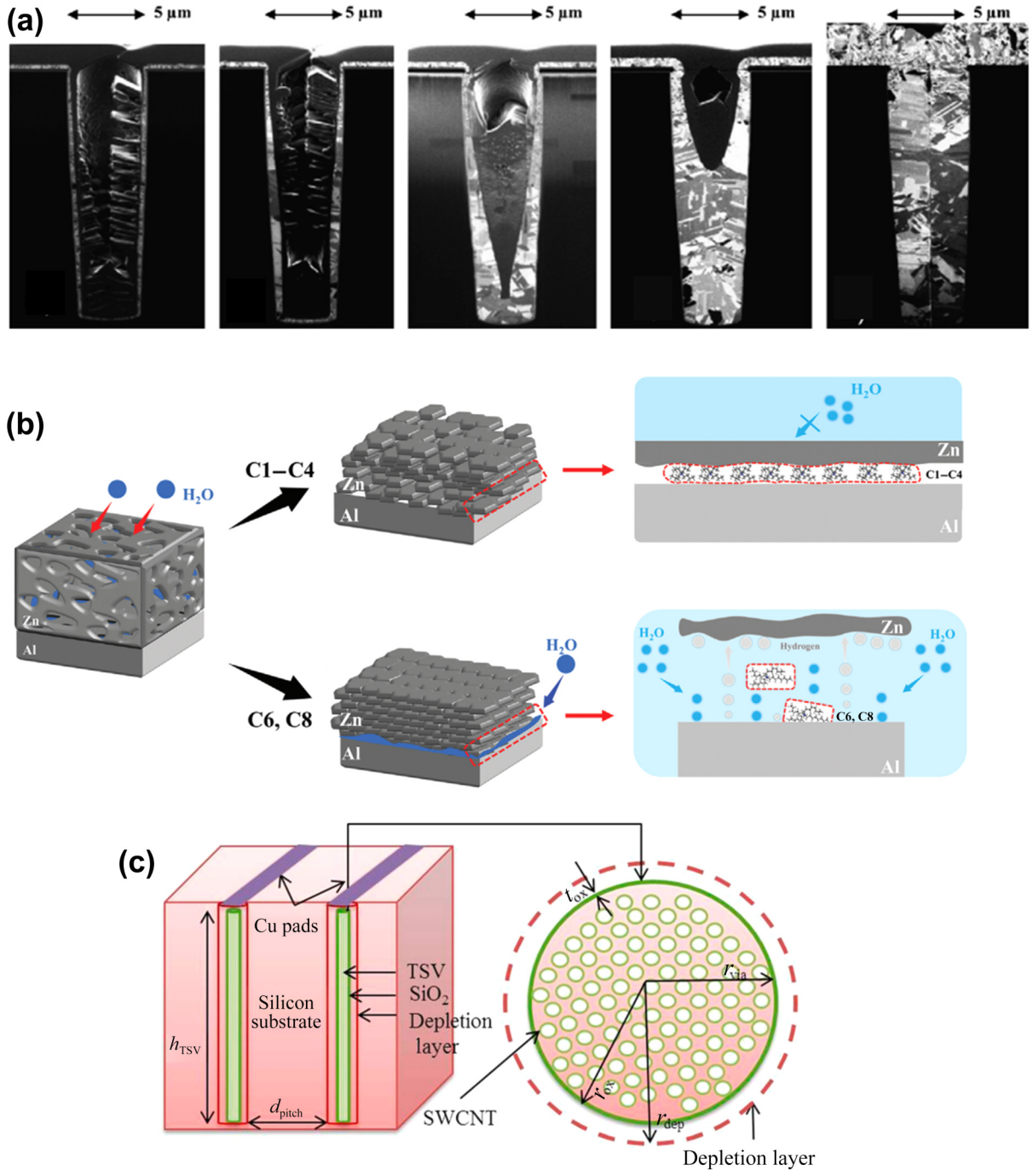


Figure 2 (a) SEM cross-sections of the vias after electrodeposition fill-up times of different times. Reproduced with permission from Ref. [30], © Elsevier Ltd. 2008. (b) Schematic diagram for HER inhibition mechanism of AAB in the electrolyte with different. Reproduced with permission from Ref. [33], © Wiley-VCH GmbH 2024. (c) Physical layout structure of TSVs.

technique for addressing moving boundary problems. By decoupling the computational mesh from the material boundary, the ALE method can effectively handle the dynamically changing geometric boundaries during the electroplating process [38]. The level set method, through the introduction of a signed distance function, can naturally handle topological changes such as the formation and closure of voids [39]. The boundary element method (BEM) exhibits unique advantages in dealing with complex geometric structures, especially in feature-scale models, as it can significantly reduce computational complexity [40].

Multiphysics coupling simulation is a current research hotspot [41]. Commercial software platforms such as COMSOL Multiphysics provide powerful multiphysics coupling solution capabilities, enabling the simultaneous solution of electric field, flow field, concentration field, and electrochemical kinetics equations. Studies have shown that through multiphysics coupling simulation, the filling process of microvias can be accurately predicted, and the simulation results are in good agreement with experimental data.

In terms of experimental verification technologies, the development of *in-situ* characterization techniques has provided

powerful tools for studying micro-nano scale phenomena [42, 43]. Scanning electrochemical microscopy (SECM) can observe the electrochemical processes on the electrode surface at the nanoscale in real time [44]. Focused ion beam (FIB) technology can prepare high-quality cross-sectional samples, and combined with scanning electron microscopy (SEM) observation, the filling morphology of microvias can be clearly displayed [30]. Synchrotron radiation X-ray imaging technology has the advantages of high resolution and large penetration depth, enabling real-time observation of the internal filling process of three-dimensional structures [45].

Electrochemical testing techniques play an important role in mechanism research. Cyclic voltammetry can investigate the electrochemical behavior of additives and reveal their action mechanisms. Galvanostatic testing can obtain the potential-time curve, from which the information related to mass transfer and reaction kinetics can be extracted. Electrochemical impedance spectroscopy (EIS) can analyze the kinetic characteristics of electrode processes and identify electrochemical processes at different frequencies [46].

3 Research on the complex mechanisms of additive action

3.1 Additive classification and molecular action mechanisms

In IC electroplating, additives are critical components for achieving high-quality metal deposition. Based on their functional characteristics, additives are primarily categorized into three types: suppressors, accelerators, and levelers. These three classes of additives interact at complex molecular levels to jointly regulate the nucleation and growth processes of metals.

A typical representative of inhibitors is PEG, whose molecular structure contains multiple ether oxygen groups. PEG achieves adsorption through the interaction between ether oxygen groups and the copper surface, forming an adsorption film on the copper surface that hinders the reduction reaction of copper ions [47]. Dow et al. found that the inhibitory effect of PEG strongly depends on its molecular weight. When the molecular weight is in the range of 6000–8000 g/mol, the Cu^{+}-PEG-Cl^{-} composite film synergistically formed by PEG and chloride ions is the densest, which can significantly increase cathodic polarization, thereby achieving the optimal inhibitory performance in microvia filling (Figs. 3(a) and 3(b)) [48].

The main components of accelerators are sulfur-containing organic compounds, such as SPS and its reduction product 3-mercaptopropanesulfonate. These molecules form strong chemical bonds with the copper surface through sulfur atoms, significantly promoting the copper deposition rate. Through cyclic voltammetry stripping (Fig. 3(c)) and X-ray photoelectron spectroscopy (XPS) (Fig. 3(d)) analyses, Chiu et al. showed that SPS dissociates on the surface of copper or gold electrodes to form MPS, which further forms a Cu(I)-MPS-Cl complex with chloride ions. This complex not only promotes the reduction of Cu^{2+} but also accelerates the oxidation of Cu^{0} to Cu^{+} during the copper dissolution process [49].

The mechanism of action of levelers is the most complex, with typical representatives including Janus green B (JGB) and imidazole-epichlorohydrin polymer (IMEP). Levelers usually contain aromatic ring structures and cationic groups, achieving adsorption on the copper surface through π–π interactions and electrostatic interactions (Fig. 3(e)) [50]. The unique feature of levelers lies in their selective adsorption property—they tend to adsorb in high current density regions (e.g., protrusions), thereby inhibiting the deposition rate in these regions and achieving surface leveling (Fig. 3(f)) [48].

3.2 Adsorption behavior in nanoscale confined spaces

Within nanoscale confined spaces, the adsorption behavior of additives exhibits characteristics markedly different from those in macroscopic systems. Due to spatial confinement effects, the conformational freedom of additive molecules is severely restricted, leading to significant alterations in their adsorption mechanisms and adsorption strengths.

Molecular dynamics (MD) simulation studies revealed the details of the adsorption behavior of additives on the copper surface. Taking SH110 as an example, this molecule contains both 4,5-dihydrothiazole (DHT) and 3-mercaptopropanesulfonic acid (MPS) groups, enabling it to bind to the copper surface through two modes. MD simulation results show that on the Cu (111) crystal plane, the DHT moiety of SH110 forms coordination bonds with the surface via nitrogen atoms and cyclic sulfur atoms, whereas the MPS moiety achieves chemical adsorption through sulfur atoms in the sulfonic acid group (Fig. 4(a)). In the nanoconfined environment of TSVs, the molecular conformation adjusts, allowing the DHT and MPS moieties to synergistically adsorb on the copper surface, significantly enhancing the interface binding strength [51].

Density functional theory (DFT) calculations provide electronic structure information on additive adsorption. Frontier molecular orbital analysis shows that the highest occupied molecular orbital (HOMO) of tetrazole derivatives is mainly distributed on the aromatic ring and nitrogen atoms, whereas the lowest unoccupied molecular orbital (LUMO) is concentrated in the sulfur-containing functional group region. For example, the HOMO of 5-hydroxy-2H-tetrazole (4b) is located on the N atoms of the tetrazole ring, and the LUMO is localized on the O and S atoms of the substituent. This electronic distribution characteristic promotes the interaction between the aromatic system and the copper surface through π-d orbital hybridization, while sulfur atoms achieve stable adsorption via strong covalent bonds, a phenomenon verified in the study by Chermahini et al. (Fig. 4(b)) [52].

In HAR microvias, the concentration distribution of additives exhibits a distinct spatial gradient. The adsorption–desorption model established by Yang et al. shows that due to the extended diffusion path, the concentration of inhibitors (e.g., PEG) at the via bottom is lower than that at the via opening, resulting in a reduced surface coverage. When the local current density exceeds the critical desorption current density, the inhibitor at the via bottom desorbs, accelerating copper deposition and thereby achieving bottom-up filling (Figs. 4(c)–4(e)). This mechanism is quantified by coupling the diffusion equation with interfacial reaction kinetics, providing a theoretical basis for the superfilling process [53].

3.3 Synergistic effects and competitive adsorption among additives

Interactions between additives are key factors determining electroplating performance, involving two fundamental mechanisms: synergistic effects and competitive adsorption. A thorough understanding of these interaction mechanisms is crucial for optimizing electroplating formulations.

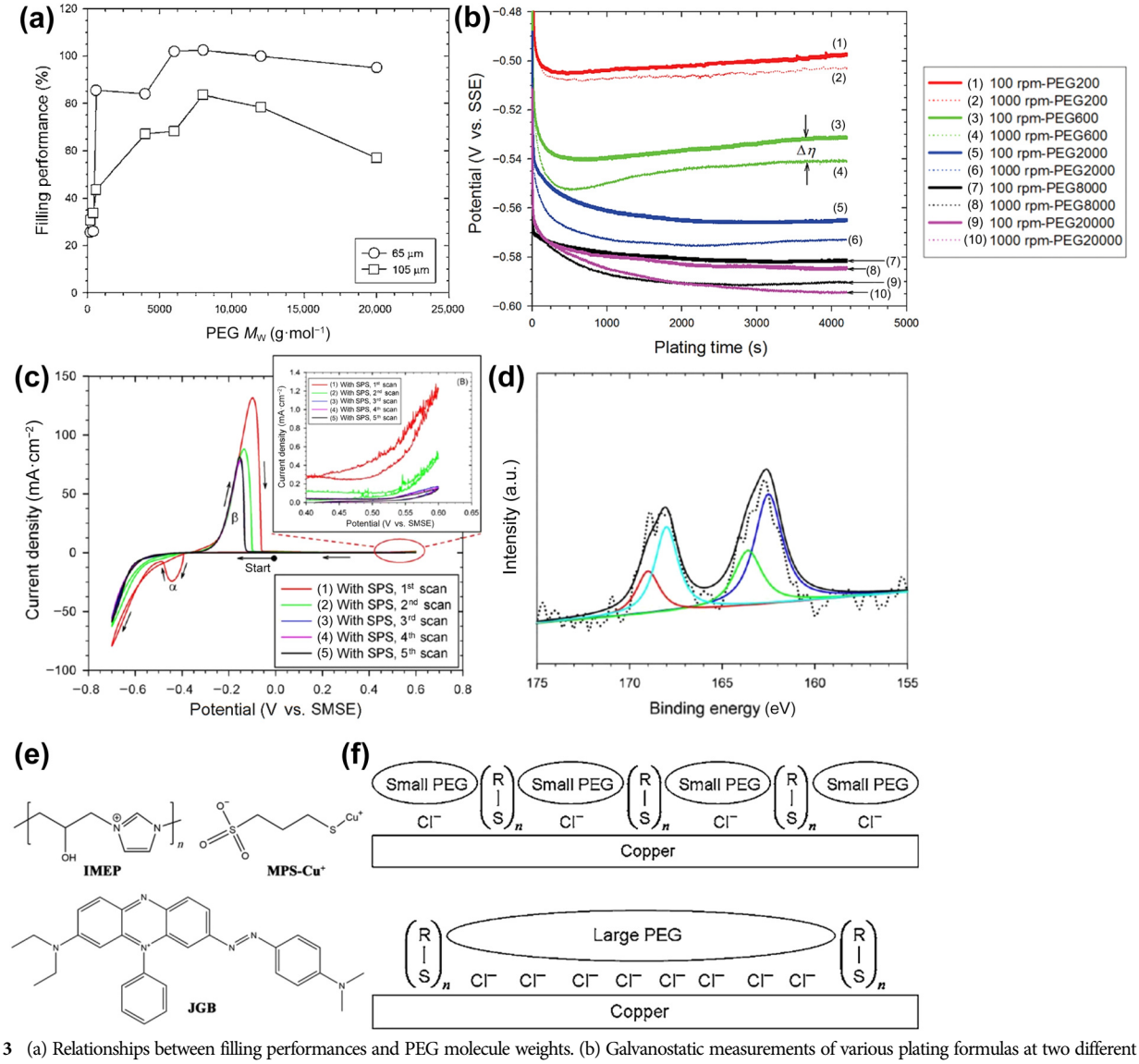


Figure 3 (a) Relationships between filling performances and PEG molecule weights. (b) Galvanostatic measurements of various plating formulas at two different forced convections. Reproduced with permission from Ref. [48], © The Electrochemical Society 2005. (c) Cu CVS on Au electrode modified by soaking in 5 mM SPS for 5 min. (d) XPS spectra in the S 2p region. Cu/Au electrode after immersion in 100 ppm SPS solution for 5 min. Reproduced with permission from Ref. [49], © American Chemical Society 2012. (e) The molecular structures of JGB and IMEP. Reproduced with permission from Ref. [50], © Elsevier Ltd. 2018. (f) Illustrations of additive adsorption on copper surface before passage of cathodic current. Reproduced with permission from Ref. [48], © The Electrochemical Society 2005.

The inhibition–acceleration interaction is the most fundamental synergistic mechanism. Studies by Ding et al. showed that when accelerators are added to electrolytes containing inhibitors, a significant acceleration effect is produced (Fig. 5(a)). The mechanism of this effect lies in the fact that accelerator molecules are small and can penetrate into the gaps between inhibitor molecules, bind to chloride ions on the copper surface, break the bonding between inhibitors and chloride ions, and lead to inhibitor desorption. With the increase of accelerator concentration, this displacement effect proceeds continuously, transforming the surface adsorption layer from inhibitor-dominated to accelerator-dominated, thereby significantly increasing the deposition rate [54].

The accelerator–leveler interaction exhibits complex competitive adsorption characteristics. Wu et al. systematically studied the interaction between commercial accelerators and levelers using chronoamperometry (CA) (Fig. 5(b)). Under low potential conditions (e.g., −0.6 V), levelers dominate the competition and inhibit the adsorption of accelerators (Fig. 5(c)); whereas under high potential conditions (e.g., −0.5 V), the situation is reversed, with accelerators occupying a dominant position (Fig. 5(d)). This potential dependence originates from the difference in electrochemical activity between different additives: Levelers typically have a higher reduction potential and are more likely to adsorb at low potentials, whereas accelerators have a lower reduction potential and can only adsorb effectively at higher potentials [55].

The inhibition–leveler interaction exhibits a unique synergistic effect. Further studies by the Wu group revealed that under conditions of high potential and low inhibitor concentration, the inhibition–leveler combination can produce a super-strong inhibitory effect (Figs. 5(e) and 5(f)). The mechanism of this synergistic effect lies in the fact that leveler molecules do not displace inhibitors but fill the gaps between inhibitor molecules, thereby increasing the surface coverage. This synergistic adsorption

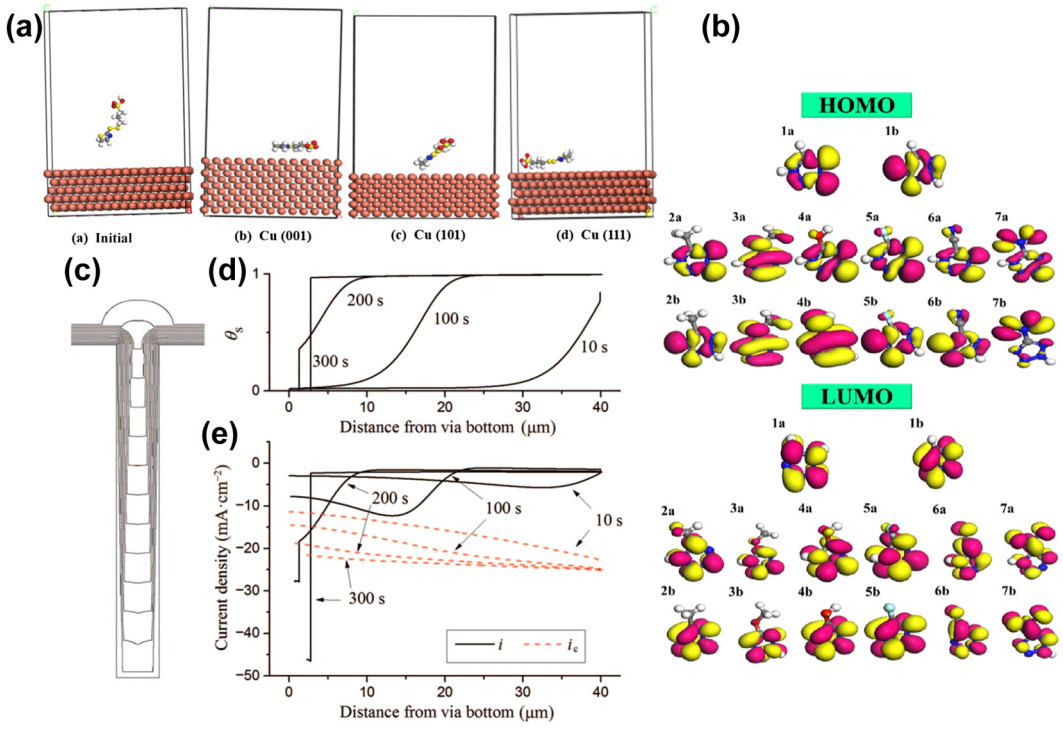


Figure 4 (a) Configuration of SH110 adsorbed on Cu (001), Cu (101), and Cu (111) surface. Reproduced with permission from Ref. [51], © Wang, F. L. et al. 2021. (b) HOMO and LUMO plots of optimized tetrazoles and their derivatives. Reproduced with permission from Ref. [52], © Esmaeilzadeh Khabazi, M. et al. 2023. Simulated results of (c) time evolution of surface profile, (d) suppressor coverage along the vertical direction, and (e) local current density i and i_c along the vertical direction for 5 μm × 40 μm TSVs plated at −3 mA·cm^{-2} average current density. Reproduced with permission from Ref. [53], © The Electrochemical Society 2013.

mode not only enhances the inhibitory effect but also improves surface uniformity, which is of great significance for achieving high-quality metal deposition [55].

3.4 Additive design philosophy and experimental validation

Based on an in-depth understanding of the mechanism of action, researchers proposed several innovative additive design concepts and experimentally validated the effectiveness of these designs.

Multifunctionalization of a single molecule is an important development direction. SH110 is a typical representative of this design concept, possessing both inhibitory and accelerating functions. SH110 acts as an inhibitor under strong convection conditions, while functioning as an accelerator under weak convection conditions. This environment-responsive characteristic enables it to automatically adjust its function according to local conditions, facilitating more uniform metal deposition. Experiments showed that using SH110 as a single additive can achieve defect-free filling of vias, simplifying process control [56].

The molecular design of polymer additives is more complex and sophisticated. Poly(1-vinylimidazole-co-1,4-butanediol diglycidyl ether) (VIBDGE) is a polymer leveler containing quaternary ammonium cations. Quantum chemical calculations and MD simulations indicate that VIBDGE achieves spontaneous adsorption on the copper surface through its unique flat-lying adsorption mode, generated nitrogen ions, and large molecular volume. Experimental verification shows that the quaternary system composed of VIBDGE, SPS, PEG, and chloride ions can significantly improve the throwing power of electroplating, verifying the correctness of the design concept [57].

Machine learning has shown great potential in additive screening and design. By establishing a relationship model between the molecular structure and performance of additives, the performance of new molecules can be quickly predicted, greatly shortening the development cycle. Studies demonstrated that MD simulations combined with machine learning methods can accurately predict the impact of additives on electroplating performance, and the prediction results are in good agreement with experimental data. This method can not only be used for the optimization of existing additives but also guide the design of entirely new additives [58].

4 Cross-scale modeling methods and challenges

4.1 Cross-scale theoretical framework and information transfer mechanisms

Addressing the cross-scale relationship between the microscopic and macroscopic is essential for elucidating the mechanisms of metal deposition behavior. This requires constructing a unified theoretical framework to seamlessly bridge different scales from atoms to reactors and achieve accurate transfer of physical information across them. The origin of this "cross-scale" nature lies in the fact that the key physicochemical phenomena determining the final deposition quality occur across vastly different spatial and temporal scales. Therefore, the core challenge in building a cross-scale model lies in: establishing a multi-physics integration framework spanning from quantum mechanics to continuum theory, creating effective information transfer channels connecting microscopic mechanisms to macroscopic properties, and ultimately achieving seamless consistency in boundary conditions and physical quantities across scales, with the aim of accomplishing full-chain accurate prediction from molecular behavior to device performance.

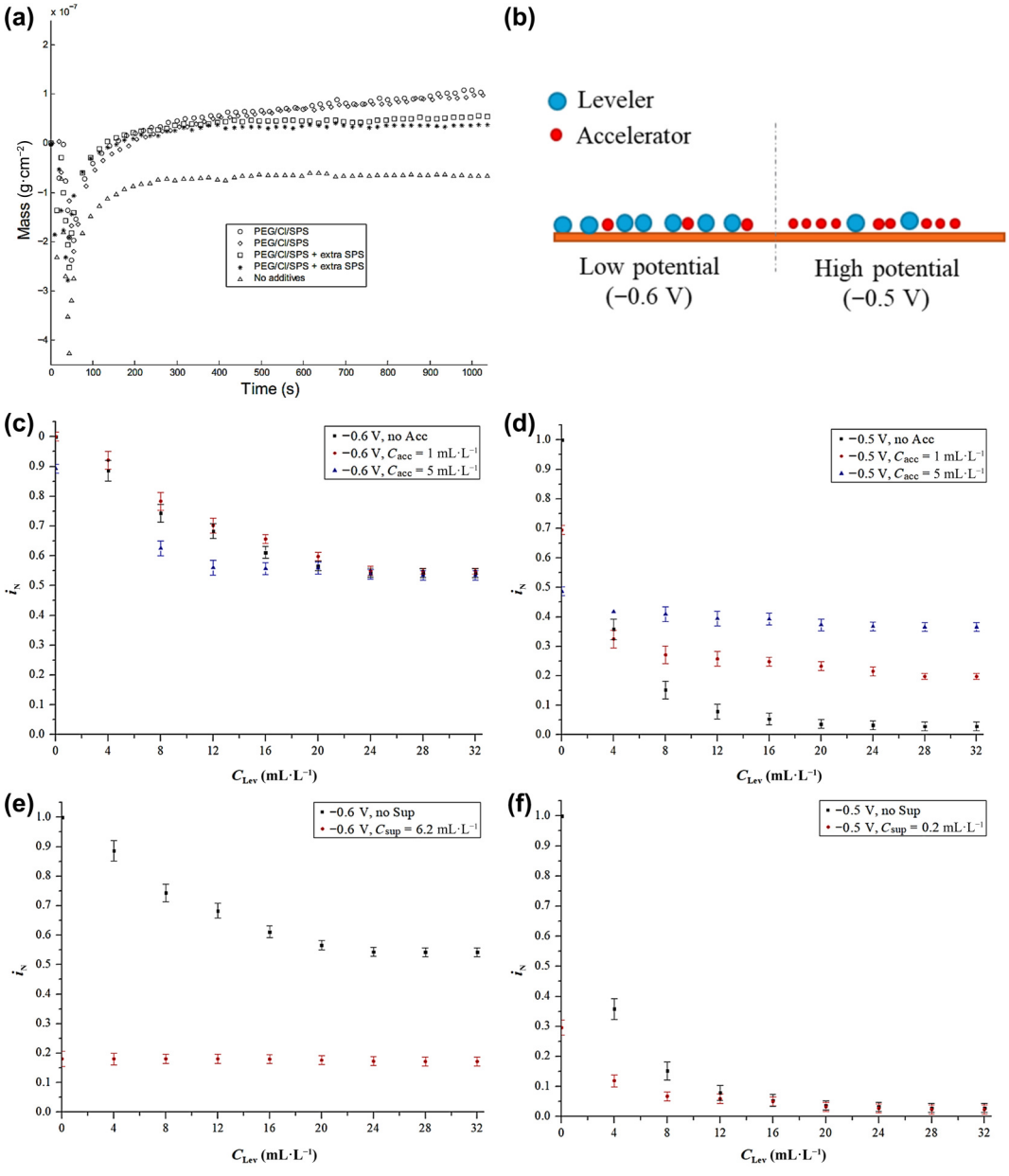


Figure 5 (a) Comparison of the mass changes on copper electrode surface during the double potential step treatment in 7.2 mol/m^3 sulfuric acid, with and without PEG/Cl$^-$/SPS. Reproduced with permission from Ref. [54], © The Electrochemical Society 2006. (b) Schematic of the interaction between leveler and accelerator. Interaction of accelerator and leveler: (c) CA measurement results of leveler injected into electrolyte premixed accelerator under low potential (−0.6 V) and (d) CA measurement results of leveler injected into electrolyte premixed accelerator under high potential (−0.5 V). Interaction of leveler and suppressor: (e) CA measurement results of leveler injected into electrolyte premixed suppressor under low potential and (f) CA measurement results of leveler injected into electrolyte premixed suppressor under high potential. Reproduced with permission from Ref. [55], © Wu, H. Y. et al. 2020.

In terms of theoretical foundation, multiscale modeling requires the integration of various physical theories. At the molecular scale, quantum mechanics methods need to be adopted to describe electronic structures and chemical bonding; at the atomic scale, MD methods are required to simulate atomic motion and interactions; and at the continuum scale, fluid mechanics, electrodynamics, and mass transfer theories must be applied to describe macroscale transport phenomena [59]. This multiphysics coupling theoretical framework must ensure the consistency and continuity of physical quantities across different scales.

The information transfer mechanism is the core challenge of multiscale modeling. Upward information transfer (from microscale to macroscale) is mainly achieved through statistical averaging methods, such as calculating stress from atomic trajectories and deriving material properties from molecular configurations. Downward information transfer (from macroscale to microscale) is realized through boundary conditions and constraints, such as transmitting macroscale conditions (e.g., temperature and pressure) to microscale models. In the electroplating process, this information transfer mechanism is particularly complex, requiring consideration of the particularity of electrochemical interfaces [60].

The selection of scale coupling methods has a significant impact on model performance. Direct coupling methods directly connect

models of different scales and achieve information exchange through iterative solution; multiscale finite element methods realize coupling by using different basis functions at different scales; and homogenization methods integrate microscale information into macroscale models through spatial averaging. Studies showed that when addressing electroplating problems, hybrid methods are often more effective, i.e., adopting the most suitable scale model for different regions and achieving coupling through interface conditions.

4.2 Multiphysics coupling solution technology

Multiphysics coupling is essential for describing the complexity of electroplating processes, involving the interaction of multiple physical fields such as electric fields, fluid flow fields, concentration fields, temperature fields, and electrochemical kinetics.

The coupling between the electric field and the concentration field is the most fundamental physical coupling relationship, and its quantitative description centers on the Nernst–Planck equation. This equation shows that the ionic flux J_i arises from three contributions: diffusion, electromigration, and convection:

$$J_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla \varnothing + c_i v \quad (1)$$

At the micro-nano scale, the reduction in characteristic size significantly enhances the role of the electromigration term. Simultaneously, the current density distribution is modulated by local concentration changes, creating a strong bidirectional coupling between the two. This coupling effect is particularly complex in HAR structures and generally requires numerical methods for solution [61].

The coupling between the flow field and mass transfer involves the simultaneous solution of the Navier–Stokes equations and the convection–diffusion equations. At the electroplating bath scale, fluid flow is mainly driven by pumping or stirring; at the feature scale, fluid flow is mainly driven by gases generated from electrochemical reactions and density changes. This cross-scale flow characteristic makes flow field modeling extremely challenging. Studies have found that inside microvias, due to the small characteristic size, inertial effects can be neglected, but electrokinetic effects such as electroosmotic flow need to be considered [62].

The coupling between electrochemical kinetics and mass transport manifests as the competition and matching between the interfacial reaction rate and the bulk mass transport process. The Butler–Volmer equation describes the fundamental relationship between the electrode reaction current density j and the overpotential η

$$j = j_0 \left[\exp\left(\frac{\alpha_a F}{RT} \eta \right) - \exp\left(-\frac{\alpha_a F}{RT} \eta \right) \right] \quad (2)$$

In practical systems, the reaction rate is also limited by reactant transport, leading to concentration polarization, which becomes particularly significant at high current densities. The consumption of reactants and the generation of products further alter the local concentration field, creating a feedback loop between kinetics and mass transport [63].

The influence of the temperature field cannot be ignored under certain conditions. Electrochemical reactions are usually accompanied by thermal effects, and especially at high current densities, Joule heating may cause a significant increase in local temperature. Changes in temperature affect the viscosity, conductivity of the electrolyte, and reaction rate, thereby influencing the entire electroplating process. Walsh pointed out that although thermal effects are significant at high current densities, in many microelectronic electroplating applications, due to the small characteristic size and fast heat dissipation, the temperature rise effect is usually limited to a low level [64].

4.3 Applications of machine learning and artificial intelligence in multiscale modeling

The rapid advancement of machine learning and artificial intelligence technologies has provided new approaches and methods for tackling multiscale modeling challenges. These technologies offer unique advantages in handling complex nonlinear relationships, large-scale data, and high-dimensional parameter spaces.

In terms of model construction, deep learning methods can automatically identify complex patterns and laws in physical processes. For example, by training on a large amount of simulation data, a direct mapping relationship can be established between input parameters (such as current density, additive concentration, and temperature) and output results (such as deposition morphology, thickness distribution, and defect type) [65]. This data-driven approach can greatly reduce reliance on physical mechanisms and improve modeling efficiency.

In terms of parameter optimization, reinforcement learning algorithms can learn optimal strategies through interaction with the environment. In electroplating process optimization, process parameters can be taken as the action space, and deposition quality as the reward function, with the optimal process window found through continuous trial and error [66]. This method is particularly suitable for handling multi-parameter and multi-objective optimization problems, enabling simultaneous optimization of multiple performance indicators.

In terms of uncertainty quantification, machine learning methods can effectively handle uncertainties in model parameters and boundary conditions. Through Bayesian methods, the uncertainty of model predictions can be quantified, providing confidence intervals for process control. This is of great significance for improving process robustness and yield [67].

In terms of cross-scale information transfer, emerging architectures such as graph neural networks (GNNs) have shown great potential. Such networks can naturally handle data with complex topological structures, such as geometric structures and concentration distributions in the electroplating process. The multi-scale Weisfeiler–Leman directed graph neural network (k-WediGNN) proposed by Zhang et al. realizes feature transfer from molecular structures to macroscale deposition morphologies by introducing a degree-oriented neighborhood aggregation mechanism, providing a new idea for cross-scale modeling [68]. By learning the mapping relationship between different scales, efficient information transfer and feature extraction can be achieved.

4.4 Advances in computational methodology and numerical techniques

Advances in computational methodology serve as a key driver for the development of multiscale modeling. New algorithms and numerical techniques continue to emerge, providing more efficient and accurate solutions for tackling complex multiphysics coupling problems.

In terms of spatiotemporal scales, the development of multi-time-scale algorithms has made it possible to handle time scales spanning multiple orders of magnitude. In the electroplating process, the fastest process is electron transfer (femtosecond scale), whereas the slowest is macroscale morphology evolution (second to minute scale). Drews et al. externally coupled the Monte Carlo method with the two-dimensional finite difference method, using different time steps to handle surface reactions and diffusion processes, and introduced a first-order digital filter to suppress numerical instability, significantly improving computational efficiency and numerical stability [69].

In terms of spatial discretization, adaptive meshing technology can automatically adjust mesh density according to changes in physical quantities. During the electroplating process, regions such as boundary layers and reaction interfaces undergo drastic changes in physical quantities and thus require dense meshes; in contrast, regions far from the interfaces have gentle changes in physical quantities and can use sparse meshes. Smallwood et al. adopted the deformed geometry module combined with unstructured meshes in COMSOL Multiphysics, successfully simulating the evolution of copper filling morphology in microvias with different aspect ratios and verifying the effectiveness of adaptive meshes in complex geometries [70]. This adaptive technology can significantly reduce computational load while ensuring accuracy.

In terms of nonlinear solution, the Newton iteration method and its variants remain the mainstream approaches, while specialized algorithms for specific problems are constantly emerging. For the stiff systems of equations in the electroplating process, Bisson et al. developed an implicit solution strategy based on the PETSc toolkit. By combining GMRES iteration with ASM preconditioning, they effectively solved the multiscale coupled model including the Nernst–Planck equation and Butler–Volmer kinetics, significantly improving the computational stability for large-scale problems [38]. The advancement of these algorithms has made it possible to solve large-scale, high-dimensional multiphysics coupling problems.

In terms of parallel computing, the popularization of graphics processing unit (GPU) computing has brought new opportunities for multiscale modeling. In the MUPHY multiscale blood flow simulation, the Bisson's group deployed the lattice Boltzmann method (LBM) and particle dynamics method on a 32-GPU cluster, achieving a near-linear speedup. The computational speed was improved by more than 10 times compared with traditional central processing units (CPUs), providing an efficient parallel scheme for multiscale particle-fluid coupling simulation in the electroplating process [71].

5 Technological trends and cutting-edge solutions

5.1 Novel electroplating process technologies

With the continuous advancement of IC manufacturing technology, traditional direct current electroplating processes have become inadequate for meeting the demands of advanced fabrication processes, leading to the emergence of various novel electroplating techniques.

Pulse electroplating technology is one of the earliest improved technologies. By periodically changing the magnitude and direction of the current, the uniformity and quality of metal deposition can be effectively improved. Pearson and Dennis systematically elaborated on the basic characteristics of pulse current, pointing out that the pulse waveform is usually jointly defined by three parameters: pulse current density (J_p), on-time (T_{on}), and off-time (T_{off}). Among these, the average current density directly affects the deposition rate, whereas the peak current density influences the cathodic overpotential and nucleation behavior. The study emphasized the potential of pulse current in regulating the coating structure, especially when using a relatively high frequency (e.g., 500 Hz) and an appropriate duty cycle (e.g., 33%–50%), it can promote grain refinement and improve coating performance. However, it also pointed out that in practical applications, the limitations of rectifier capacity and double-layer capacitance on high-frequency pulses need to be comprehensively considered [72].

Pulse reverse electroplating is an emerging technology that introduces a reverse current phase based on traditional pulse electroplating, regulating the deposition uniformity inside vias through periodic anodic dissolution. Ge et al. systematically studied the effects of reverse pulse parameters (including frequency, duty cycle, and current density) on the filling quality of HAR vias. They found that when the reverse current density is 10% of the forward current density (e.g., 0.2 $A{\cdot}dm^{-2}$), the duty cycle is 20%–40%, the frequency is 100 Hz, and void-free and ultra-uniform copper filling can be achieved. Additionally, the coating exhibits a strong (111) texture, which is conducive to improving interconnect reliability (Figs. 6(a)–6(c)). This technology dissolves the over-deposited copper at the via opening through reverse current, alleviates concentration polarization, and thereby significantly enhances the metal distribution uniformity in the deep via region [73].

Ultrasonic-assisted electroplating technology utilizes the cavitation effect and mechanical vibration of ultrasonic waves to improve mass transfer and surface conditions. Zhao et al. confirmed through numerical simulations and electrochemical experiments that under ultrasonic conditions of 120 kHz and 200 W, the average flow velocity of the solution inside microvias is significantly increased, the thickness of the diffusion layer is reduced by approximately 64.1%, and the limiting diffusion current density is increased to 11.78 $A{\cdot}m^{-2}$, thereby significantly promoting the transport and uniform deposition of metal ions inside microvias (Figs. 6(d) and 6(e)). Studies have shown that ultrasonic cavitation can effectively remove adsorbed bubbles and surface impurities, while promoting grain refinement, and exhibits superior adaptability especially in the filling of HAR microvias [28].

5.2 *In-situ* monitoring and feedback control technology

The development of real-time monitoring and feedback control technologies has made precise process control achievable. These technologies can capture process status information in real time and automatically adjust process parameters based on preset quality standards.

In terms of monitoring technologies, a variety of advanced detection methods have been applied in the electroplating process. EIS can monitor the kinetic characteristics of electrode processes in real time, and the deposition quality and process status can be judged by analyzing changes in the impedance spectrum [46]. Linear sweep voltammetry (LSV) can monitor potential changes during electroplating, extracting information related to nucleation and growth. Current noise analysis can detect abnormal phenomena during deposition, such as dendrite growth and bubble evolution.

Optical monitoring technologies provide non-contact detection

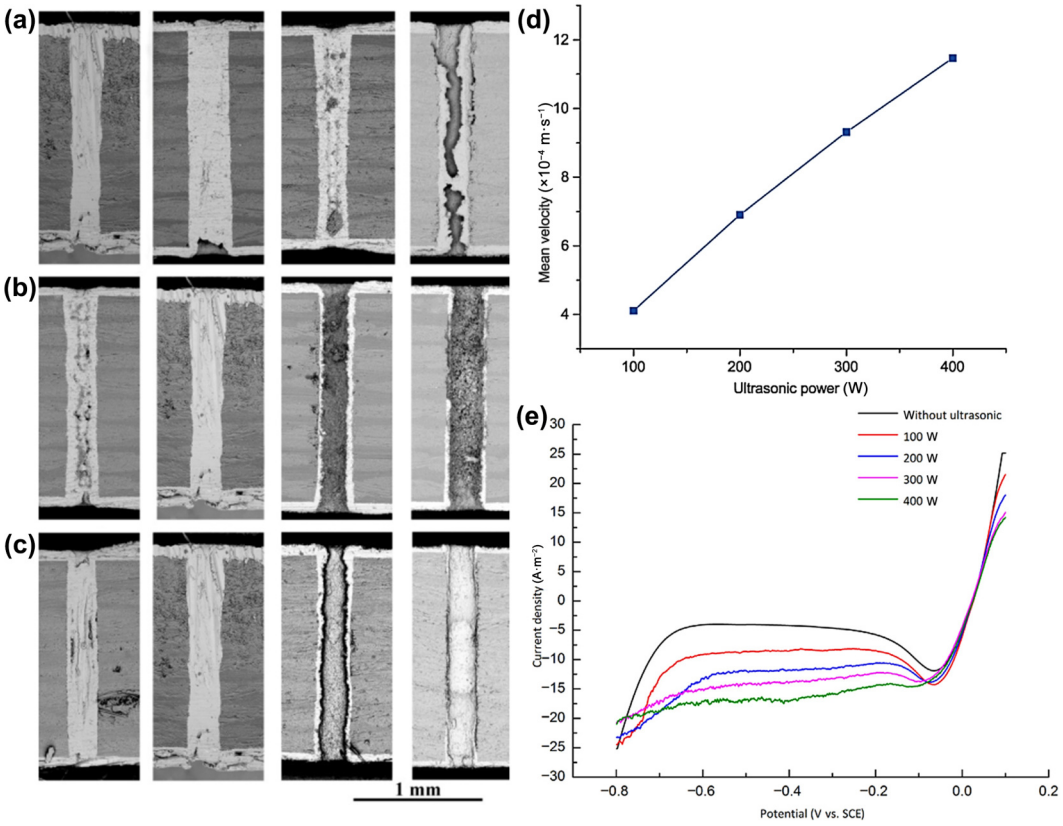


Figure 6 Cross-sectional observations of the filled PTH by PPR plating. (a) Reverse pulse frequency (Hz). (b) Reverse pulse duty cycle. (c) Reverse pulse current density (A·dm^{-2}). Reproduced with permission from Ref. [73], © Ge, W. et al. 2022. (d) Mean velocities inside microvias with different ultrasonic powers. (e) Mean velocities inside microvias with different ultrasonic powers. Reproduced with permission from Ref. [28], © Elsevier B.V. 2018.

methods. Optical microscopy can observe the evolution of surface morphology [74]; spectroscopic techniques can analyze surface composition and structure [75]. The advantage of these technologies lies in their ability to achieve *in-situ* and real-time monitoring without affecting the normal process.

X-ray imaging technology has unique advantages in the internal monitoring of 3D structures. Synchrotron radiation X-ray microscopy can achieve 3D imaging with micrometer-level resolution, enabling real-time observation of the filling process of complex structures such as TSVs [76]. This technology can not only detect the final filling quality but also observe the dynamic evolution of the filling process, providing important information for process optimization.

The core of the feedback control system is to establish a relationship model between process parameters and quality indicators. Through machine learning methods, complex nonlinear mapping relationships can be established to achieve intelligent process control. For example, based on real-time monitored current and voltage signals, the deposition quality can be predicted, and parameters such as current density and temperature can be automatically adjusted to ensure quality consistency [77].

5.3 Exploration of new material systems

The exploration of new material systems offers innovative approaches to addressing challenges in electroplating technology. These novel materials not only enhance the performance of existing processes but also hold the potential for revolutionary technological breakthroughs.

Alloy electroplating technology can obtain properties that a single metal cannot achieve by co-depositing two or more metals during the electroplating process. For example, copper-nickel alloys exhibit excellent electromigration resistance, making them particularly suitable for high-temperature applications; and copper-cobalt alloys can control magnetism by adjusting their composition, which is valuable in certain special applications [78]. The key challenge of alloy electroplating is to realize the co-deposition of different metals, which requires precise control of the reduction potential and deposition rate of each component.

Composite electroplating technology introduces solid particles into the electroplating process, enabling particles to co-deposit with metals to form composite materials. Commonly used particles include CNTs, graphene, and ceramic particles. Studies showed that the addition of CNTs can significantly improve the mechanical strength and electrical conductivity of copper [79]; graphene can enhance the lubricity and corrosion resistance of the coating [80]; and ceramic particles can increase hardness and wear resistance [81]. The main challenge faced by composite electroplating is to ensure the uniform dispersion and stable suspension of particles.

Organic–inorganic hybrid materials represent a new direction in material design. Such materials combine the flexibility of organic components and the rigidity of inorganic components, possessing unique properties. For example, electroplating systems containing ionic liquids can achieve the electroplating of certain refractory metals at room temperature [82]; and polymer electrolytes can provide better film-forming properties and uniformity [83].

The development of functional additives is another important direction. In addition to the traditional functions of inhibition, acceleration, and leveling, novel additives can also realize special

functions, such as antibacterial activity, self-healing, and conductivity regulation [84]. These functionalized additives provide possibilities for the development of new electroplating processes.

5.4 Process integration and equipment innovation

Process integration and equipment innovation are key factors driving the industrial application of electroplating technology. Process integration simplifies manufacturing workflows and enhances production efficiency, whereas equipment innovation enables higher process precision and improved repeatability.

In terms of process integration, "one-stop" electroplating solutions are becoming a development trend. Such solutions integrate multiple process steps into a single equipment, including cleaning, activation, electroplating, and post-treatment. The advantages of integration lie in reducing the handling and waiting time to improve production efficiency, avoiding contamination during intermediate steps, and achieving better process control. For example, some advanced electroplating equipment has integrated ultrasonic cleaning, chemical treatment, electroplating, and detection functions, enabling the completion of the entire electroplating process in one equipment [85].

Equipment innovation is mainly reflected in the following aspects: First, the improvement of temperature control technology, precise temperature control, can enhance process stability and reproducibility. Second, the optimization of stirring systems, novel stirring technologies, can achieve more uniform flow field distribution. Third, the innovation of electrode systems, including improvements in electrode shape, material, and arrangement. Finally, the intellectualization of control systems, adaptive control, is realized through the introduction of artificial intelligence technology.

In terms of intelligent manufacturing, electroplating equipment is developing towards digitization, networking, and intellectualization. By integrating various sensors and actuators, precise control of process parameters can be achieved; through data analysis and machine learning, process optimization and fault prediction can be realized; and via remote monitoring and cloud platforms, centralized management and maintenance of equipment can be accomplished.

The concepts of standardization and modular design are also driving equipment innovation. By establishing standardized interfaces and protocols, interconnection and intercommunication between different devices can be achieved; and through modular design, equipment can be quickly configured and upgraded according to different needs. This design concept not only reduces equipment costs but also improves the adaptability and maintainability of equipment.

6 Conclusions and outlook

This study systematically analyzes three core issues regarding the metal nucleation and growth mechanisms across the nano-micro-macro scales in the field of electronic electroplating for IC: the mass transfer and electric field distribution at the micro-nano scale, the complexity of additive action mechanisms, and the challenges in multiscale model construction. Through in-depth theoretical analysis, numerical simulation, and experimental verification, the following main research results have been achieved:

In terms of micro-nano scale mass transfer and electric field distribution, the mechanism of uneven electric field distribution in HAR structures was revealed, and it was found that the ratio of current density at the via bottom to that at the via opening can reach 13:1; the variation law of mass transfer mechanisms across multiple scales was clarified, confirming that diffusion dominates the mass transfer process when the aspect ratio is greater than 1; and a multiphysics coupling simulation platform based on the ALE method and the level set method was established, enabling accurate prediction of the electroplating process in complex geometric structures.

In terms of additive action mechanisms, the molecular mechanisms of inhibitors, accelerators, and levelers were systematically clarified; the unique characteristics of additive adsorption behavior in nanoconfined spaces were revealed; the synergistic effects and competitive adsorption mechanisms between additives were analyzed in depth, and it was found that the inhibitor-leveler combination can produce a super-strong inhibitory effect under specific conditions; and multiple novel additives were developed based on the molecular design concept, verifying the feasibility of multifunctionalization of a single molecule.

In terms of multiscale modeling methods, a cross-scale theoretical framework from quantum mechanics to continuum mechanics was established; a machine learning-based multiphysics coupling solution technology was developed; a multiscale information transfer mechanism suitable for the electroplating process was proposed; and the GPU-accelerated large-scale parallel computing was realized, improving the computational efficiency by 1-2 orders of magnitude.

Looking ahead, the development of electronic plating technology for IC will face both greater opportunities and challenges:

In terms of basic research, it is necessary to further deepen the understanding of electrochemical interface phenomena at the nanoscale, especially the influences of quantum effects and surface effects; develop more accurate multiscale theoretical models to achieve a true unified description across scales; and explore new experimental characterization technologies to realize *in-situ*, real-time, and multiscale observation of the electroplating process.

In terms of technological innovation, artificial intelligence and machine learning technologies will play a greater role in process optimization and quality control; the exploration of new material systems will bring more breakthrough progress; and process integration and intelligent manufacturing will drive industrial upgrading.

In terms of technical economics, it is necessary to establish a process optimization system that balances both performance and cost, particularly focusing on the cost-effectiveness balance between novel additives and traditional systems; there is a need to develop low-cost multi-physics simulation and AI optimization tools to lower the technical entry barriers for small and medium-sized enterprises; and it is essential to explore green and environmentally friendly recycling and reuse technologies for electrolytes to achieve synergistic effects of emission reduction and cost reduction.

In terms of application expansion, with the development of 3D integration technology, the requirements for electroplating technology will continue to increase; and new application fields such as flexible electronics and bioelectronics will provide new development opportunities for electroplating technology.

In terms of industrialization challenges, it is necessary to address the compatibility of new processes with existing production lines, particularly low-cost adaptation solutions for equipment retrofitting; it is essential to improve the yield stability of high-

aspect-ratio structure filling, addressing the superimposed effects of multi-parameter fluctuations during mass production; and there is a need to develop efficient online detection and feedback control technologies to meet the real-time quality control requirements of large-scale production.

In summary, the research on multiscale metal nucleation and growth mechanisms in electronic electroplating for IC is a complex systematic engineering involving interdisciplinary intersections. Only through continuous basic research, technological innovation, and engineering practice can the development of this field be continuously promoted, providing strong support for the progress of IC manufacturing technology. Future research needs to strengthen international cooperation, integrate advantageous resources from different fields, jointly tackle key technical challenges, and drive the entire industry towards a higher level of development.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work. Author Lei Wang is the editorial board member of this journal, but he is not involved in the peer-review or decision of this article.

Author contribution statement

L. W. and J. P. L. supervised the research. J. P. L. conceived the research. W. X. X. collected documents, sorted out materials, and wrote original manuscripts. Z. L. L., N. W. L., Y. J. G., and Z. L. C. helped supervision, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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