Review article

Erik Hagen Waller* and Georg von Freymann

From photoinduced electron transfer to 3D metal microstructures via direct laser writing

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Abstract: We review the fundamental concepts of direct laser writing (DLW) of 3D metallic structures via photoreduction and give an overview over the state-of-the-art. On the one hand, metallic microstructures and nanostructures play an important role in photonic applications such as resonators, antennas, metamaterials, and polarizers. On the other hand, DLW offers a flexible and fast way to fabricate microstructures. Because the underlying mechanisms from the first photoreaction to the final 3D microstructure are quite complex and not yet well controlled, we believe that a review of the photochemistry and photophysics of the direct writing process of metal structures helps to promote development in this field. To this end, we first summarize the principles of electroplating and electroless plating as this helps understand the photoresist's components. Next, we describe the different photoreducing agents and photoreactions that lead to metal seeds and in consequence to nanoparticles. This is followed by insights into the physics of nanoparticle agglomeration to the desired microstructure. Finally, we give an overview over the state-of-the-art of DLW metallic 3D microstructures.

Keywords: direct laser writing; metamaterials; metal microstructures; photoreduction.

1 Introduction

There exists a manifold of applications of metallic microstructures: from electrical wires and electrodes in, for example, electro-optic modulators or microelectromechanical systems (MEMS) [1–3], via metallic surfaces in which microstructures may lead to well-designed frictional and wear properties [4, 5], to structured magnets that are employed in spintronics [6]; often, metallic structures are among the key components of a functional device [7]. In photonics, especially metamaterials and plasmonic devices benefit from the properties of, for example, silver and gold. Hereby, multilayer structures and 3D spatial microstructuring are becoming increasingly important [8, 9].

A recent excellent review focuses on additive metal fabrication techniques capable of producing less than 10 μm feature sizes in a one-step process [10]. Some of the discussed manufacturing techniques, however, have crucial disadvantages: traditional subtractive methods, selective laser or electron beam melting, direct ink writing, electrohydrodynamic printing, laser-induced forward transfer, and meniscus-confined electroplating, each being excellent methods of choice for certain structures, are not suited for arbitrary structure designs or limited in maximum resolution, preventing their use as a rapid prototyping system. Electrophoretic deposition, electroplating of dispensed ions in solution, and focused electron beam-induced deposition are able to produce high-quality structures; however, they are intrinsically slow (less than 10 $\mu\text{m/s}$).

Contrary to the named techniques, direct laser writing (DLW; also called 3D printing) via multiphoton absorption allows for 3D structures of high quality with feature sizes less than 100 nm [11–16] and writing speeds of several centimeters per second. Briefly, a laser beam is focused into a photosensitive material that in the strongly localized focal volume causes the material to change. By translating the substrate or by scanning the beam in 3D trajectories, almost arbitrary 3D structures may be fabricated.

*Corresponding author: Erik Hagen Waller, Physics Department and State Research Center OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany, e-mail: ewaller@rhrk.uni-kl.de

Georg von Freymann: Physics Department and State Research Center OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany; and Fraunhofer Institute for Industrial Mathematics ITWM, 67663 Kaiserslautern, Germany

To create 3D metallic structures via DLW, up to now, most commonly an inverse polymer template is produced. Next, the metal structure is galvanically grown and, finally, the polymer is calcined or etched away [17]. Although the quality of structures obtained this way is high, the additional processing steps lead to higher complexity, to longer processing times, and to a limited choice of substrates (as the latter needs to be conductive). Furthermore, not all designs are possible using such postfabrication filling processes as the electrolyte may be blocked from reaching all desired positions.

Direct photoreduction does not require these additional steps, does not limit the choice of substrate, and thus has the potential to enable the fabrication of, for example, complete MEMS with a single technology. It is based on the (multi)photon-induced reduction of dissolved metal precursors to neutral metal atoms and subsequent agglomeration of these atoms to a metal structure. A number of groups already demonstrated that this procedure is possible in principle [18–21]. Unfortunately, up to now, few of the directly written metal structures show a quality rivaling those of polymer or galvanically grown structures, preventing their application in photonics. This is mostly due to so far not completely controllable thermal, light-matter interaction and chemical processes that take place during fabrication. Novel resists that do not suffer from these drawbacks are thus highly desirable.

DLW has mostly been applied in the physics community, whereas photoreduction is mainly chemical in nature. Our motivation for this review is bringing together the two communities by providing the reader with an overview over relevant principles and underlying theory, cover challenges, desirable structure properties from a physicist's point of view, and the state-of-the-art. We thus hope to provide the tools to push development in the field. The paper is organized as follows: we first cover the principles and theory of conventional DLW and redox reactions in Sections 2 and 3. We do not consider DLW from the gas phase [22], as this process is not easily incorporated in nowadays commercially available DLW systems. Next, the complete process is covered in Section 4 starting from the photoinitiation, via reaction pathways after excitation and nucleation and growth, to light-matter interaction. Examples from the recent literature and exemplary calculations further illustrate the importance of the covered theory. Finally, we identify selected publications in which the DLW of metal structures is demonstrated. We report on the measures that are employed to overcome various challenges (Section 5). An outlook wraps up this review.

2 Principles of DLW

DLW as understood today is a 3D microstructuring technology with a typical setup containing a laser source, some means to modulate the average intensity such as an acousto-optic modulator, a microscope objective, and 3D stages. In conventional systems, a near-infrared wavelength pulsed laser beam (typically $\lambda = 780$ nm) is focused by a high numerical aperture (NA) objective (NA = 1.4) into a photoresist that is transparent at the wavelength used (e.g. IP resists, Nanoscribe GmbH, or SU-8, MicroChem Corp.). Within the resist, photoinitiators with a nonnegligible two-photon absorption cross-section are present. The probability for two photons being absorbed simultaneously by the initiator molecules is proportional to the square of the incident intensity. Due to tight focusing by the high NA objective, usually a few milliwatts of average power (for an 80 MHz, ≈ 150 fs system) are sufficient to allow for substantial two-photon absorption within the focal volume. Generally, upon excitation, the initiators trigger a chemical reaction that then leads to either formation of bonds (e.g. polymerization in negative tone resists) or breaking of bonds (e.g. decomposition of solubility inhibitors in positive tone resists). Thus, moving the focal spot within the resist on 3D trajectories allows almost arbitrary 3D structures to be fabricated (typical writing speeds are about centimeters per second). Often, these structures are subsequently revealed by a development step. The key advantages of this technique are due to the nonlinear dependence of the absorption on incident intensity: the excited volume pixel is much more confined and hardly any reduction of the excitation intensity by absorption is present when structuring deep in the volume of the resist.

In a conventional DLW setup, metallic structures may be fabricated by a two-photon initiated reduction process, for example, via photoreducing agents. The principles of such redox reactions in electrolytes are discussed in the following section.

3 Principles of redox reactions and electrolytes

In its most generalized definition, reduction is the uptake of electrons by a molecule, the electron acceptor. In contrast, oxidation is defined as the loss of electrons. These reactions take place simultaneously and they are then termed redox reactions.

Reduction, either electrically or electroless, is a well-known process to deposit highly uniform layers of metal

or metal composites onto almost arbitrary surfaces [23, 24]. Metal precursors (usually salts such as Ag^+Cl^-) are hereby reduced to a neutral metal (e.g. Ag^0). In electroplating, this reduction occurs at the cathode, which thus restricts the method to conductive substrates. In electroless plating, reduction takes place via electron transfer reactions [25, 26]. Heat may provide the necessary energy for the reaction to take place and certain chelating agents prevent an undesired reduction in the volume. Electroless plating thus tends to be chemically more involving than electroplating.

As silver is of high importance for nanophotonics applications, all examples are correspondingly given in this section. However, the principles covered here are generic and can be extended to other metals as well.

3.1 Deposition

The deposition of metals is grouped into electrodeposition and electroless deposition; both, however, usually are redox processes [27] (and thus follow similar underlying mechanisms, especially as two-photon reduction processes):

The two processes are distinguished by the electron source: during electrolysis, electrons provided by the cathode reduce metal ions; thus, deposition predominantly takes place at this cathode; in electroless processes, electrons are transferred during chemical reactions without an external electron source. Electroless reactions may further be grouped into surface reactions in which electrons are provided by the surface to be coated and thus only allow very thin coatings and into noncontact reactions that make use of a reducing agent (R^{n+}) being oxidized [27]:

The latter type of electrolyte is very interesting for DLW purposes as it is largely independent of the substrate. This is highly desirable for the fabrication of 3D metallic microstructures from the user's point of view.

3.2 Reduction potential

Besides the metal source and the reducing agent, in a typical electroless plating solution but also in novel DLW

resists suitable for metal microstructure fabrication, complexants, buffers, accelerators, and stabilizers (explained below) are present [23]. In such complex chemical systems, the question arises which molecules or atoms are oxidized and which are reduced. The answer is found in the reduction potential of a substance (see Table 1 [28]): if a substance is placed into a liquid, the solvation (or hydration) pressure leads to the substance's ions going into solution, which charges the substance [29]. The solvation pressure is counteracted by the osmotic pressure that leads to ions being incorporated into the lattice and thus to positive charging until a dynamic equilibrium occurs. For example, the following half-reaction may take place:

leading to net positive charging. Material properties determine the equilibrium potential $E^{(0)}$. Smaller ionization-, bond-, and lattice-energy and larger solvation free enthalpy reflect in larger solvent pressure (see Born-Haber thermodynamic cycle; Figure 1A), whereas, for example, higher ion concentration increases osmotic pressure [30]. Therefore, the standard potential $[\Delta E^{(0)}]$ is introduced as a measure for the tendency of a chemical species to be reduced at standard conditions (solutes at 1 M concentration or gases at 1 atm pressure). It is determined by the potential difference between the equilibrium potential of a substance placed into a 1 M solution of its solutes (e.g. silver in a 1 M silver chloride solution) and the equilibrium potential at a H_2 flooded hydrogen reference electrode (standard hydrogen electrode, SHE) in 1 M HCl solution for the respective half-reaction (at 25°C). For example, a substance with low ionization energy easily gives up (binding) electrons and therefore easily goes into solution, leading to a more negative standard potential. In consequence, strong reducing agents have a very negative standard potential and reduce all substances with higher

Table 1: Standard potentials for selected half-reactions at 25°C referenced to the SHE [28].

Half-reaction	$\Delta E^{(0)}$
$\text{Au}^+ + e \rightarrow \text{Au}$	+1.69 V
$\text{Au}^{3+} + 3e \rightarrow \text{Au}$	+1.50 V
$\text{Ag}^+ + e \rightarrow \text{Ag}$	+0.80 V
$\text{Cu}^+ + e \rightarrow \text{Cu}$	+0.52 V
$\text{H}^+ + 2e \rightarrow \text{H}_2$	± 0.00 V
$\text{Ni}^{2+} + 2e \rightarrow \text{Ni}$	-0.26 V
$\text{Fe}^{2+} + 2e \rightarrow \text{Fe}$	-0.45 V
$\text{Ti}^{3+} + 3e \rightarrow \text{Ti}$	-1.37 V
$\text{Na}^+ + e \rightarrow \text{Na}$	-2.71 V

Figure 1: Contributions to the reduction potential.

(A) Thermodynamic Born-Haber cycle: transfer of a metal ion from the metal to the electrolyte [30]. Various contributions to the free enthalpy change and thus to the reduction potential of a substance need to be considered when designing an electrolyte. (B) Simplified Pourbaix diagram for the silver/water system [31], visualizing conditions for thermodynamically stable phases and phase transitions. Dashed lines represent the upper and lower boundaries for stable water.

standard potential. Sodium, for example, is a strong reducing agent, whereas noble metals are not [32].

The standard potential is defined in 1 M solutions. However, when designing a novel resist for metal DLW, standard conditions are usually not suitable. Furthermore, the free enthalpy change, the driving force behind the above electron transfer processes, depends on the activities of all oxidants and all reductants in the solution. Via $\Delta G = \Delta G^{(0)} + RT \ln(Q)$, where Q is the reaction quotient and $\Delta G = -zF\Delta E$, the reduction potential for nonstandard conditions is determined by the Nernst equation [32, 33]:

$$\Delta E = \Delta E^{(0)} - \frac{RT}{zF} \ln \left[\prod_{i=1}^k a_i^{\nu_i} \right], \quad (5)$$

where R is the gas constant, T is the temperature, z is the number of transferred electrons, F is the Faraday constant, a_i is the activity, and ν_i is the stoichiometric coefficient of substance i . Concentration-independent substances (e.g. solids) have an activity of 1. The stoichiometric coefficient is negative for the oxidation half-reaction (o) and positive for reduction half-reaction (r) of a redox equation. Furthermore, for sufficient dilution ($<10^{-2}$ mol/l), the activity may be set equal to the concentration of the respective substance (c_o , c_r):

$$\Delta E = \Delta E^{(0)} + \frac{RT}{zF} \ln \left[\frac{\prod_{o=1}^l c_o^{\nu_o}}{\prod_{r=1}^m c_r^{\nu_r}} \right]. \quad (6)$$

For example, the redox reaction, $\text{Ag}(\text{NH}_3)_2^+ + 2\text{H}^+ + e \rightleftharpoons \text{Ag}_s + 2\text{NH}_4^+$, leads to the following concentration dependence of the reduction potential [with $a(\text{Ag}_s) = 1$]:

$$\Delta E = \Delta E^{(0)} + \frac{RT}{zF} \ln \left[\frac{[\text{Ag}(\text{NH}_3)_2^+][\text{H}^+]^2}{[\text{NH}_4^+]^2} \right]. \quad (7)$$

Clearly, any redox reaction that directly or indirectly involves H^+ or OH^- ions is pH dependent. This dependence is usually visualized in Pourbaix diagrams [34, 35]. These diagrams are deduced from the Nernst equation and plot the equilibrium potential between thermodynamically stable phases of ionic and neutral metal as well as its oxidized species. They furthermore allow to extract conditions for respective phase transformations (Figure 1B [31]) and thus guide the resist designer in choosing an optimal combination of photoreducing agent and pH.

Redox reactions are usually split in their respective half-reactions to determine the tendency of net reaction to occur. For example, $2\text{AgNO}_3 + \text{Zn} \rightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{Ag}$ is split into the reduction part $2\text{Ag}^+ + 2e \rightarrow 2\text{Ag}$ ($\Delta E_{1/2}^{(0)} = +0.80$ V) and into the oxidation part $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e$ ($\Delta E_{1/2}^{(0)} = +0.76$ V). In this case, the net reaction has a positive standard potential of +1.56 V and thus may occur spontaneously. Any possible competing redox reaction with a lower net potential is less likely to take place. In addition, reversing the reaction direction means reversing the sign of the individual half-reactions and thus for the above reaction leads to a total potential of -1.56 V, which indicates that the energy

needs to be put into the system to drive the reversed reaction.

3.3 Components of electrolytes

Besides metal precursors, reducing agents, and solvents, most electrolytes for electroless deposition but also resists suitable for DLW of metallic microstructures contain complexants, buffers, accelerators, and stabilizers, as described below.

3.3.1 Metal source and complexants

The metal source usually consists of metal complexes. These have a central metal ion that, due to its nonfully occupied orbitals, bonds to ligand molecules, or ions that in turn have at least one free electron pair [36]. They form a coordinative bond with the total number of attachments being the coordination number. The stability of these complexes for the same metal ion depends on the chelate effect [37]. Ligands such as ammonia, water, or chloride may only bind at one site, whereas, for example, ethylenediamine (en) binds at up to two sites and forms chelate complexes. The latter tends to be dramatically more stable as during their formation less entropy of disorder is lost. For example, the stability constant for the formation of $[\text{Ni}(\text{en})_3]^{2+}$ is several orders of magnitude larger than for $[\text{Ni}(\text{NH}_3)_6]^{2+}$. However, other factors also influence stability [37]. Silver, for example, favors a linear arrangement of ligands [38]. Ligand molecules not only determine the stability of a complex but also solubility and reduction potential [39–42]. Thus, to tune the electrolyte or resist properties, ligand exchange reactions that enhance or reduce the stability, solubility, and reduction potential of a metal complex may be necessary. It must be ensured, however, that these complexing agents do not react with the reducing agent or retard the oxidation of the reducing agent. The effect of the complexant on the reduction potential may again be calculated by the Nernst equation. Under ligand saturation conditions, we get [39]:

$$\Delta E = \Delta E^M + \frac{RT}{zF} \ln \frac{K_o}{K_r}, \quad (8)$$

where ΔE^M is the reduction potential of the respective metal ion if no ligand is present, $K_o = [\text{M}][\text{L}]/[\text{ML}]$ and $K_r = [\text{M}^-][\text{L}]/[\text{M}^-\text{L}]$. As a rule of thumb, less electronegative ligands lead to a metal complex that is more easily

oxidized compared to their more electronegative counterparts and vice versa [42].

3.3.2 Reducing agent

As discussed in the previous section, reducing agents are the electron-donating substance and thus tend to have very negative reduction potentials. Typical reducing agents include formaldehyde for silver and copper reduction as well as hydrazine, sodium hypophosphite, or sodium borohydride for the reduction of ionic nickel to neutral nickel, nickel phosphite, or nickel boride, respectively, [23, 27]. Photoactive reducing agents are described in detail in Section 4.

3.3.3 Stabilizers, capping agents, or surfactants

In addition to complexants for ligand exchange reactions, stabilizers or capping agents are added to the electrolyte. Stabilizers such as polymeric polyvinylpyrrolidone (PVP) and polyvinyl alcohol adsorb to dust and other active nuclei and thus shield them from the electrolyte by steric forces [23, 43, 44]. Surfactants have hydrophobic and hydrophilic groups that lead to an electric double layer (forming micelles and reverse micelles) on the surface of particles [43]. These additives thus prevent (further) spontaneous reduction at the particle surface (e.g. PVP at the surface of silver nanoparticles). Not to prevent deposition at desired positions, the concentration of stabilizers should be low enough, however. Furthermore, stabilizers play an important role during metal particle growth (see Section 4.3).

3.3.4 Buffers or pH regulators

For reduction processes that directly or indirectly involve hydrogen or hydroxyl ions, the pH changes during the reaction. This alters the reaction conditions and may even cause the reaction to cease. Buffers, such as ammonia for alkaline conditions or carboxylic acids for acid conditions that do not take part in the reduction process besides capturing or releasing hydrogen or hydroxyl ions, are used to prevent pH value changes during deposition [23].

3.3.5 Accelerators or exaltants

Accelerators increase the reaction rate without increasing electrolyte instability. These are usually anions such

as glycine or fluoride ions that act as sacrificial electron donors, thus quickly reduce the oxidized reducing agent to its original state, and therefore make it available for further reduction [23].

4 Principles of light-induced fabrication of metal microstructures

Photoreduction and electroless reduction are very similar in their principle processes. However, instead of reduction taking place at some potentially pretreated surface or spontaneously in the whole solution, photoreduction is triggered via one-photon or multiphoton absorption of laser radiation by molecules in solution (Section 4.1). The excited molecules either have a different reduction potential than their ground-state equivalents or undergo a chemical reaction with the products of the reaction then providing the necessary reduction potential. After excitation, the reaction proceeds in a similar fashion as in electroless plating: the metal precursor is locally reduced to neutral metal atoms (Section 4.2). These atoms then agglomerate to form metallic particles (Section 4.3).

In its most basic form, a typical photoresist therefore constitutes the following components: photoreducing agent, electron donor, and metal precursor in solution. All three components could be a single molecule if upon excitation an intramolecular electron transfer takes place (photodissociation of a metal complex). Although this potentially reduces the complexity of the resist, even then, the photoreduction process is highly dynamic with the concentration of constituents changing and the evolving particles further interacting with light. Thus, in the remainder of this section, we give a detailed review of the principles of photoreduction, growth and agglomeration, and interaction of particles with light.

4.1 Photoinitiation

The fabrication of 3D structures requires a threshold behavior during some step of the photoinduced process. The threshold originates during the initiation process due to multiphoton or residual absorption, potentially combined with quenching, inhibition, and nonlinear growth processes [45]. In any case, the photoactive component plays a major role. Apart from direct photoreduction of a metal source via ligand to metal charge transfer, a number of different types of photoreducing agents have been

employed or may potentially be employed to initiate photoreduction: organic dyes and photoinitiators [43] as well as metal [46], semiconducting [47], and hybrid semiconductor-metal nanoparticles [48]. They have in common that after excitation they may either directly or indirectly provide electrons via intermediate reactions for the reduction half-reaction or at least accelerate this reaction by being heated.

The excitation of a molecule leads to a different electronic distribution compared to the molecule's ground-state distribution. In the excited state, higher orbitals are occupied with the electrons' average probability density of position being farther away from the nuclei. Thus, the excited-state molecule displays completely different chemical and physical properties. For example, ionization energy is lowered and electron affinity is increased in magnitude, making excited-state molecules a stronger reducing and, potentially at the same time, oxidation agent than its ground-state equivalent [49]. Chemical reactivity also changes, as most chemical reactions are considered to be electron transfer processes that in turn are more probable for less tightly bound electrons [50]. Intermolecular and intramolecular energy transfer may be enhanced due to increased electron-electron interaction. Furthermore, bond lengths and bond angles may change after excitation; thus, selectivity for certain reactions may alter. Usually, the first singlet and triplet states are of interest, as those have a sufficiently long lifetime to make electron or energy transfer probable [49].

Only little data are available on excited-state reduction potentials of photoreducing agents or radicals suitable for DLW. Until such a database is available, the estimates below give some guidance for choosing a photoreducing agent.

4.1.1 Excited-state photoreducing agents

The excited-state reduction potentials of a molecule may be determined by phase-modulated voltammetry [51] and estimated from its ground-state potentials (deduced from the Gibbs energy of photoinduced single electron transfer) [49]:

$$\Delta E_{\text{red}}^* = \Delta E_{\text{red}} + \Delta E_{01} / e + w \text{ (reduction potential),} \quad (9)$$

$$\Delta E_{\text{ox}}^* = \Delta E_{\text{ox}} - \Delta E_{01} / e + w \text{ (oxidation potential).} \quad (10)$$

ΔE_{01} is usually determined from spectroscopic data and corresponds to the energy gap between the excited state and the ground state (each in its lowest vibrational level,

measured in joules). w is a solvent-dependent electrostatic work term that originates from Coulombic attraction between products and reactants but in most cases may be omitted due to its small contribution [49].

Note that due to their higher ΔE_{01} singlet states have stronger reduction potentials than the corresponding triplet states; however, the latter usually has substantially longer lifetimes, making electron transfer more probable [49].

4.1.2 Photocatalysts

From the excited state, a molecule may either participate in intermolecular or intramolecular electron or energy transfer or undergo radiative quenching. Photosensitizers or light-absorption sensitizers transfer their energy or experience a quenching cycle (see the next subsection) to return to their ground state (often energy and electron transfer are indistinguishable and energy transfer may be viewed as two electron transfer). Thus, sensitizers are not consumed. They play the role of catalysts.

4.1.3 Photoinitiators

Contrary to photocatalysts, photoinitiators, photoacid generators, or photobase generators upon excitation produce new reactive species such as radicals [21], photoacids [52, 53], or photobases [54, 55] via photolysis and they are thus consumed. Although the initiator itself may not be a reducing agent in a given resist, its products, however, may lead to reduction. For example, a radical strives to give up an electron to change to a closed-shell configuration, whereas photobases facilitate ligand deprotonation.

4.1.4 Initiation by photodecomposition

The direct photodissociation of a metal source has long been applied in the DLW of metal structures from the gas phase [56–58] or liquid phase [18]. Closely related, as it is a photodecomposition process, is using ligand-covered nanoparticles [59, 60] as a starting material and removing the ligand by excitation.

4.1.5 Nanoparticles

Semiconducting nanoparticles or quantum dots may be designed to yield almost arbitrary energy gaps. For a

spherical particle with diameter D , the band gap may be estimated by the Brus model [61, 62]:

$$\Delta E_{\text{qd}}(D) = \Delta E_{\text{b}} + \frac{\hbar^2 \pi^2}{2D^2} \left[\frac{1}{m_{\text{e}}^*} + \frac{1}{m_{\text{h}}^*} \right] - J_{\text{e-h}}(D) + 0.285 E_{\text{Ry}}^*, \quad (11)$$

where ΔE_{b} is the bulk band gap, $J_{\text{e-h}}$ is the total Coulomb energy of the electron-hole pair, $m_{\text{e,h}}^*$ is the effective mass of electrons or holes, respectively, and E_{Ry}^* is the exciton Rydberg energy. The self-polarization energies of electron and hole have been omitted. The semiconductor physics community references the electron energy to the vacuum level, whereas the SHE is used as reference in electrochemistry [63]. Hereby, 0 V on the SHE scale corresponds to -4.5 eV on the vacuum scale. Therefore, the Fermi level in the electrolyte referenced to the vacuum level is calculated by $E_{\text{F}} = -e\Delta E^{(0)} - 4.5$ eV. When brought into contact, the Fermi levels of the semiconductor and the electrolyte must be equal, which determines the positions of the conduction band edge and the valence band edge on the SHE scale (with the conduction band edge lying on the negative side of the SHE scale and the valence band on the positive side edge) [64]. Changing the size allows controlling the light absorption properties of the quantum dot but also influences reduction potentials. However, surface defects and adsorbed or bound molecules play a major role in determining a quantum dot's reduction potentials. Thus, the dot's potential may independently be tuned by functionalization with ligands, covalently bound molecules and especially by metal nanoparticles [65, 66]. The latter allows a fast intrinsic charge separation, which is advantageous compared to mere metal or mere semiconducting nanoparticles. Furthermore, metal nanoparticles may be used as seeds that strongly enhance growth processes (see Section 4.3).

4.2 Electron transfer and reaction pathways after excitation

After the excitation of the initiator or the metal complex, radiative or thermal energy dissipation may take place. For reduction, electron transfer is required. Note that the speed and the quantum yield of electron transfer are relevant parameters that finally limit the fabrication speed in DLW.

For radical-based reduction, the bond cleavage of the initiator molecule (which itself may be viewed as an electron transfer process, described by the intramolecular dissociative-electron transfer theory [25]) occurs after excitation, creating radicals with loosely bound electrons

and low reduction potential. The electron may then tunnel from the radical to the metal source; however, it needs to overcome an activation barrier that stems from the change of electronic configurations of the reaction partners as well as the rearrangement of solvent cages or ligands [67].

Photocatalysts or nanoparticles transfer electrons without the formation or breakage of bonds in an outer sphere transfer process. Marcus' theory efficiently approximates the rate constant of the single electron transfer [26]:

$$k_{\text{et}} = A \exp \left[-\frac{(\lambda + \Delta G^{(0)})^2}{4\lambda k_B T} \right], \quad (12)$$

where A mainly is determined by the reaction partners' overlap of the electronic wave functions, λ is the reorganization energy required for rearrangement of atomic, electronic orbital, and molecular positions of all involved molecules, and the intrinsic barrier free enthalpy $\Delta G^{(0)}$ is related to the reduction potentials of the reaction partners. Clearly, for high rate constants, it is not sufficient to select reaction partners to obtain a maximal exergonic electron transfer (Marcus inverted region [68]). However, the rate of electron transfer tends to be larger, the greater the overlap between initial and final molecular wave function (the lower the need for atomic rearrangement) is. As the atomic arrangement of rigid molecules such as $\text{Ru}(\text{bpy})_3$ does not depend on the oxidation number, these tend to be good catalysts for fast electron transfer [69].

Contrary to radicals, catalysts via a sacrificial electron donor, regain an electron and regenerate the ground-state catalyst to fulfill a complete oxidative quenching cycle (Figure 2A [49]). Thus, for photoredox catalysts, the dynamics and the net outcome (net reductive, net oxidative, or net redox-neutral [49]) of the overall reaction need to take the full cycle into account and thus require the careful choice of the sacrificial electron donor.

Other oxidants may lead to parasitic quenching of the excited-state photoreducing agent and prevent the reduction of the metal precursor. For example, under aerated conditions and in water-based solutions, the following half-reactions may compete with the desired redox reaction [28]:

These reactions are favored compared to any reaction with a lower potential versus SHE. Therefore, for example, the reaction $\Delta E^{(0)}(\text{Au}^+ + \text{e} \rightarrow \text{Au}) = +1.83 \text{ V vs. SHE}$ is easily possible in water, whereas $\Delta E^{(0)}(\text{Ni}^{2+} + 2\text{e} \rightarrow \text{Ni}) = -0.25 \text{ V vs. SHE}$ is suppressed until all H^+ ions and dissolved O_2 molecules are consumed. To some extent, this may be desired as it provides a chemical threshold for the DLW process. Note the pH dependence of especially Equations (13) and (15) that lead to the water lines in Figure 1B and the role of oxygen in Equations (14) and (15). Thus, by adjusting pH and by deaerated conditions, the threshold may be controlled.

4.3 Nucleation, growth, and agglomeration

Ideally, after photoreduction, a large number of metal atoms are present in the solution. According to the LaMer model (Figure 2B), if these atoms locally surpass a critical concentration, nucleation, which is the phase change from dissolved to solid metal, occurs and nuclei evolve [70, 71]. The new phase, however, is metastable. The classical nucleation theory predicts a critical seed radius above which seeds remain solid. After nucleation, these seeds grow with the growth mechanisms potentially being quite complex encompassing diffusion-controlled growth, Oswald ripening, and coalescence or aggregation. In the end, these steps are crucial in the outcome of the DLW microstructure: the size distribution of the evolving particles influences the surface roughness and porosity of the structure; furthermore, nucleation and growth rates influence fabrication speed.

4.3.1 Classical nucleation theory

The classical nucleation theory is a thermodynamic model: a phase change from atoms in solutions to atoms in a cluster decreases the free energy (ΔG_v) proportionally to the number of atoms or likewise the volume of the cluster [70]. This, however, is counteracted by the surface term γ . This term is thermodynamically costly, as atoms at the surface have less entropy than atoms in solution as well as an energetically unfavorable arrangement compared to bulk atoms. The surface energy is thus proportional to the surface area (Figure 2C). The total free energy of a spherical particle with radius r therefore becomes [70]:

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v, \quad (16)$$

Figure 2: Post excitation processes.

(A) Oxidative quenching cycle of a catalyst [cat] excited by photons. The catalyst reduces a metal ion $[M^+]$ to neutral metal $[M]$ and is oxidized. The oxidized catalyst returns to its original state after being reduced by a sacrificial electron donor. (B) Scheme of the evolution of nucleation according to the LaMer model. (I) Increase of neutral metal concentration by reduction. (II) At a concentration of C_{crit} , the activation barrier of nucleation is overcome leading to rapid self-nucleation (burst nucleation). The concentration of neutral metal is thus quickly reduced and lowered below C_{crit} and terminates nucleation. (III) Diffusion-controlled growth further reduces the concentration and finally leads to a constant level. (C) Scheme of the surface (ΔG_s) and volume (ΔG_v) term of the cluster free energy ΔG . The maximum free energy a nucleus has during nucleation ΔG_{crit} is reached at the critical radius r_{crit} . This radius corresponds to the minimal size a nucleus needs to have to remain stable in solution. (D) Scheme of the interaction potential of two nanoparticles. The interaction potential W_{tot} is the sum of the van der Waals potential W_{vdW} and the electrostatic interaction potential W_{EDL} due to the electrical double layer.

$$\Delta G_v = \frac{-k_B T \ln S}{v}, \quad (17)$$

$$\frac{dN}{dt} = A \exp\left(-\frac{\Delta G_{crit}^{homo}}{k_B T}\right), \quad (18)$$

where S is the super saturation of the solution and v is the molar volume. From this equation, the maximum free energy change ΔG_{crit}^{homo} and a critical radius r_{crit} of a nucleus may be derived by differentiation with respect to r (also see Figure 2C). The latter gives the minimum radius a nucleus must obtain not to redissolve. The first may be considered as an activation barrier for nucleation. It thus leads to Arrhenius-type rate equations for nucleation [70]:

where the pre-exponential factor A is related to the rate of atom or molecule attachment and thus proportional to their diffusivity in solution [72].

Heterogeneous growth is nucleation on the surface of an existing seed. The new nuclei no longer have a spherical shape but form a contact angle with the seed. This reduces the surface term and thus the critical activation barrier [70]:

$$\Delta G_{crit}^{hetero} = \Phi \Delta G_{crit}^{homo}, \quad (19)$$

with Φ only dependent on the contact angle. This explains the dramatically faster nucleation rate in the presence of seeds compared to homogeneous nucleation.

4.3.2 Growth mechanisms

After nucleation, a number of different potentially multistep growth mechanisms lead to nanoparticles of different sizes, size distributions, and crystalline properties. Thus, altering reaction conditions and stabilizers during this step, one obtains some control of the final particle.

In the classical growth theory, growth is governed by two mechanisms: surface reactions (in our case reduction) with a reaction rate k and diffusion with a diffusion constant D [70]. Both are concentration dependent, which leads to the following growth rate [70]:

$$\frac{dr}{dt} = \frac{Dv(C_b - C_r)}{r + D/k}, \quad (20)$$

where C_b is the concentration of solute in the bulk solution and C_r is the solubility of the particle. The latter is related to the particles size by [70]

$$C_r = C_b \exp\left(\frac{2\gamma v}{rk_B T}\right). \quad (21)$$

This dependency on particle size influences the size distribution of the final particles. Oswald ripening may occur where small particles redissolve easier and thus allow larger particles to grow further, leading to a narrower size distribution [70]. The change of the standard deviation $d(\Delta r)/dt$ may be calculated from Equation (20). For predominantly diffusion-controlled reactions, this leads to [70]

$$\frac{d(\Delta r)}{dt} = \frac{2\gamma D v^2 C_b \Delta r}{k_B T \bar{r}^2} \left(\frac{2}{\bar{r}} - \frac{1}{r^*} \right), \quad (22)$$

where $\bar{r}$ is the mean particle radius and r^* is the particle radius in equilibrium within the bulk solution. The regime where $d(\Delta r)/dt < 0$ is the Oswald self-sharpening regime and obtained when super saturation is high ($\bar{r}/r^* > 2$). For a predominantly surface reaction-controlled growth, such a regime does not exist. In this case, the change in size distribution is always positive [70]:

$$\frac{d(\Delta r)}{dt} = \frac{2\gamma k v^2 C_b \Delta r}{RT \bar{r}^2}. \quad (23)$$

4.3.3 Agglomeration and aggregation

A further growth mechanism is the reversible agglomeration or irreversible aggregation of particles to a larger colloid. This growth process is governed by particle interaction forces, for nonmagnetic identical particles mainly the attractive van der Waals force and due to overlapping electrical double layers repulsive electrostatic forces [71, 73, 74]. The respective interaction potentials are both proportional to particle size but show a different decay over particle distance. The combination of these two interactions as described by DLVO theory (established by Derjaguin, Landau, Verwey, and Overbeek) leads to an energy barrier (see Figure 2D) that defines the stability of a colloid. The barrier height is usually larger for larger colloids and thus larger colloids tend to be more stable than smaller colloids. Other forces may also play a role: for particles in close contact (closer than a few nanometers), repulsive steric forces, hydrophobic, solvation, and capillary forces need to be taken into account (non-DLVO forces). Thus, the total free energy of interaction is usually extended to [71]

$$G = G_{vdW}^+ + G_{elec-stat}^- + G_{non-DLVO}^\pm, \quad (24)$$

where + stands for attractive, – stands for repulsive, and $\pm$ stands for potentially attractive or repulsive potentials.

4.3.4 Stabilizers

Stabilizers such as PVP play a major role during the growth process of metallic nanoparticles as they influence, for example, steric and capillary forces [74]. Furthermore, in their role as capping agents, they may prevent further growth of particles by adsorbing to the seed surface and thus stabilize the particle. Thermodynamically speaking, size control is achieved by reducing the surface free energy and thus the critical radius [44, 75]. They may selectively adsorb to certain crystal planes as in the case of PVP that predominantly adsorbs to the 100 facet via its carbonyl group, whereas thiol group-containing capping agents do not show this selectivity [75]. This leads to a large number of potential shapes (cubes, spheres, wires, etc.) for the fundamental building blocks of a metal microstructure.

4.3.5 Light-particle interactions

Scattering and absorption cross-sections of spherical nanoparticles are proportional to the particle's radius to the sixth and third power, respectively, [76]. Although small

seeds do not influence light much, after growth especially absorption potentially leads to a number of nonnegligible effects [77]: absorbed energy may lead to hot electrons on the particle surface initiating further redox reactions [46, 64], field enhancement may take place at edges triggering directed growth [78, 79], and thermal heating may alter reaction kinetics. Similarly, the gradient force of optical trapping and the scattering force are also, respectively, proportional to the third and sixth power of the particle radius; thus, optical trapping also plays an increasingly important role [60, 80]. Finally, melting point depression, the reduction of the melting point (T_m) of a particle with radius (r), needs to be considered using the Gibbs-Thomson equation [81]:

$$T_m = T_{bm} \left(1 - \frac{c}{r} \right), \quad (25)$$

where T_{bm} is the bulk temperature and c is a constant dependent on the solid-liquid interface energy, the bulk heat of fusion, and the solid-phase density. For example, a silver nanoparticle with a diameter of 3 nm has a melting point less than half the melting point of bulk silver [82].

5 DLW of 3D metal microstructures: challenges and state-of-the-art

Photoreduction is a promising technique to fabricate nanophotonic structures. A large number of groups have applied the above principles to fabricate metallic

nanoparticles of various sizes and shapes with potential applications in plasmonics [43, 83, 84]. Some have produced 2D structures for electronic or photonic purposes (see, for example, [85, 86]). For example, Figure 3 shows a split-ring resonator array designed by Lu et al. for an optical response in the terahertz regime [86].

Only few groups have extended this technique to 3D structures (mainly [18–21, 87–89]). Truly 3D structures remain challenging: reduction and nucleation at the substrate-resist interface usually show a completely different behavior compared to within the volume. Particle-light interaction leads to uncontrolled growth. Nucleation and adsorption rates may be too low to allow for connected 3D lines, as particles may diffuse before adsorbing to an existing structure and gas evolution by reaction products (e.g. chloride when using a silver chloride precursor) may deteriorate the structure.

Different 3D photoreduction-based fabrication approaches that tackle these challenges are found in the literature. In this review, we focus on those methods. Other reviews exist that cover different aspects of state-of-the-art fabrication of 3D metal structures: Farahani et al. and Hirt et al. focus on different, including non-DLW, fabrication techniques [10, 90], whereas Barner-Kowollik et al. give an overview over the challenges of functional photoresist development but do not focus on metal DLW [91]. A very recent article by Tabrizi et al. provides a good introduction into two-photon reduction and extensively covers applications of thus fabricated metal microstructures [92]. Because progress in the field has been somewhat slow, however, we feel that a review focusing on the guidelines for resist design and fabrication strategies complements the above papers very well.

Figure 3: Direct laser written THz-metamaterials.

(A) Scanning electron microscopy (SEM) image of a split-ring resonator array made of gold with a scan speed of 2 μm/s and a laser power of 1.57 mW. (B) Corresponding measured terahertz response of the resonator array showing the feasibility of the photoreduction technique for the fabrication of nanophotonic structures. Reprinted with permission from Ref. [86]. Copyright 2013, Optics Materials Express.

5.1 Desirable photoresist and microstructure properties

Before discussing published strategies to overcome the challenges of metal DLW, we state the properties an ideal resist should have and the properties the final microstructure should have from the user's point of view.

On the top of the list of wishes of properties an ideal resist would have is a large two-photon or multiphoton quantum yield and thus selectivity for the respective reaction when excited by photons with 780 nm wavelength. Energy that does not contribute to the reaction should quickly dissipate out of the system without causing adverse side reactions. One-photon absorption should not take place in the visible for the resist to be processable in standard optic laboratories. In liquid resists, reaction and nucleation rates as well as growth rates should be high to allow for high fabrication speeds. Long shelf life and especially constant reaction conditions during fabrication should be ensured (e.g. volatile solvents avoided). Processability with conventional technologies (e.g. spin coating), simple postexposure treatment, and easily disposable components are a plus.

The properties the final microstructure should have largely depends on the application: in micro-optics, surface roughness should be less than $\lambda/10$ (thus less than ≈ 40 nm in the visible), whereas in some applications a high surface area and high porosity may actually be beneficial (e.g. electrodes). Most users, however, require their microstructure to have properties close to the respective bulk material (or at least they feel more comfortable if this is the case): in electronics and plasmonics, usually conductivity close to the values of the respective bulk material

are desired whereas in microengineering mechanical properties such as hardness should match.

5.2 Substrate adaptation

At the substrate-resist interface, the intensity threshold for the reduction reaction usually is dramatically lower compared to the threshold in the volume. This is on the one hand due to the lower activation barrier for heterogeneous nucleation (Section 4.3) at surface imperfections and on the other hand due to the surface being activatable. For example, our experiments have shown that sputtering 3 nm of iridium on a glass substrate reduces the threshold for silver reduction to approximately half compared to reduction on a mere glass substrate (most likely due to heating or hot electron generation). However, if modification of the substrate becomes necessary, the versatility of the fabrication method is lost; thus, the following routes are more promising: in an early publication on 3D direct metal writing [18], the large threshold difference was tackled by simply increasing the incident laser power for all features sufficiently far away from the interface. Figure 4A shows a silver structure where the two poles were fabricated with an average laser power of 18.8 mW, whereas the top was fabricated with 29.8 mW both with a scan speed of 24 $\mu\text{m/s}$ (excitation wavelength 800 nm and repetition rate 80 MHz). The photoresist was an aqueous solution of silver nitrate without any additional photoreducing agent. Later on, photoinitiators were added to lower the threshold within the resist. Figure 4B shows silver structures that were fabricated by Ishikawa et al. with the aid of the photoinitiator Coumarin 440. In this

Figure 4: Influence of the substrate.

(A) SEM image of a 3D pure silver structure fabricated without the aid of additional photoreducing agents at a scan speed of 24 $\mu\text{m/s}$. Reprinted with permission from Ref. [18]. Copyright 2006, Applied Physics Letters. (B) Likewise, for silver structures fabricated with Coumarin 440 as photoinitiator. Reprinted with permission from Ref. [19]. Copyright 2006, Applied Physics Letters.

case, the whole structure was fabricated at a laser power of 18.85 mW. Still, the authors, due to convection and turbulences, experienced fluctuating conditions above the substrate compared to directly at the interface. Thermal heating also was found to be an issue [19].

Note that choosing a photoreducing agent is challenging: it should not directly reduce the precursor in its ground state but do so efficiently in its excited state or via its reaction products. Therefore, looking at Equation (10), it is clear that being able to choose the excitation wavelength is very beneficial and relaxes some constraints on the photoreducing agent.

5.3 Thermal-input control

Two sources responsible for heating exist: absorption of the laser and the exothermic reaction. Most work is done on reducing the contribution of the first to heating. Ideally, all absorbed energy is converted to chemical energy (which, however, is impossible as always reorientation of solvent molecules requires a share of the energy). Photoreducing agents with a high quantum yield make the reduction process more energy efficient and thus less photons are needed. This leads to less parasitic photons being absorbed by particles in the photoresist and therefore to less heating. For example, Ishikawa et al. have shown two different writing regimes for low and high incident power in the photoresist described in the previous subsection [19]. Less than 5 mW reduction is driven by two-photon absorption, which allows good control of the linewidth, whereas more than 5 mW reduction is thermally driven (Figure 5A). Already, most publications use ultra-short pulse lasers to avoid heat accumulation. Blasco et al. showed that reducing the repetition rate from 4 MHz via 500 kHz to 100 kHz improved structure quality

even more (Figure 5B [21]). In their photoresist, a water-soluble polymer [acrylate-functionalized poly(ethylene glycol) and acrylic acid] and the likewise soluble photoinitiator Irgacure 2959 were added to the aqueous solution of HAuCl_4 . The excitation wavelength was 700 nm, the scan speed was $2.5 \mu\text{m/s}$, and the average laser power was typically 0.2 mW.

Even with the above tricks, some heating is unavoidable due to the exothermic nature of the reaction. Substrates and resists with high thermal conductivity and large heat capacity aid in reducing its impact. For this reason, water-based resists are beneficial and most commonly employed [18]. Note, however, that water-based resists are not index matched to oil immersion microscope objectives conventionally used in DLW; thus, the NA may be limited by total internal reflection. Also, aberrations severely distort the excitation mode when structuring deep inside the volume of an index-mismatched resist.

5.4 Structure morphology

The critical radius and the particle size distribution determine the surface roughness of the obtained structures (Section 4.3). For small but stable features, many small particles with a narrow size distribution are beneficial. Therefore, surfactants or stabilizers are commonly employed. Small, sub-500 nm linewidth was shown, for example, by Cao et al. [20], Xu et al. [85], and Lu et al. [86] using *n*-decanoylsarcosine sodium (NDSS), trisodium citrate (and its reduction products), and ionic liquids as stabilizers, respectively. Note that not only linewidth but also surface roughness are reduced (Figure 6A and B).

The influence of stabilizers is, however, difficult to predict, as they often play multiple roles in a resist. PVP,

Figure 5: Influence of thermal-input.

(A) Different initiation processes: at high laser, power thermal initiation dominates; at low laser, power initiation is photon triggered.

Reprinted with permission from Ref. [19]. Copyright 2006, Applied Physics Letters. (B) Quality improvement of gold-polymer composite lines by the reduction of the repetition rate from 500 to 100 kHz. Reprinted with permission from Ref. [21]. Copyright 2016, Advanced Materials.

Figure 6: 2D metallic structures.

SEM images of lines written with the aid of stabilizers: low surface roughness using (A) trisodium citrate and (B) ionic liquids (top: ionic liquid has a short carbon chain length; bottom: ionic liquid has a large carbon chain length). Reprinted with permission from Refs. [85] and [86]. Copyright 2010 and 2013, Small and Optics Materials Express, respectively. (C) Microexplosions occur with PVP as stabilizer. Altering fabrication parameters influences morphology: (D) reduced scan speed leads to broader but more compact structures (left: 300 $\mu\text{m/s}$ and right: 20 $\mu\text{m/s}$) and (E) scanning a line multiple times increases granularity (left: 3 scans and right: 12 scans). (D and E) Reprinted with permission from Ref. [93]. Copyright 2002, Applied Surface Science.

for example, also enhances viscosity of the resist, leading to less efficient thermal convection and thus to microexplosions as seen in Figure 6C.

Besides the above chemical approach to adjust structure morphology, writing parameters may also influence morphology: for example, Wang et al. showed that reduced scan speed seems to give a more compact if broader copper line, whereas scanning a line multiple times increases the granularity of the line (Figure 6D and E [93]). They used 532 nm excitation wavelength and a commercially available copper solution.

In contrast, structure quality benefits if in addition to the pulsed excitation laser a second, continuous wave laser of lower wavelength aids the reduction process. He et al. showed that an excitation wavelength of 780 nm and a support wavelength of 442 nm lead to a low surface roughness of about 10 nm of silver structures and was attributed to the trapping force exerted by the second laser, which keeps the particles close together [94]. Their 2D structures were fabricated at a maximum writing

speed of 3.5 $\mu\text{m/s}$ and a minimum average excitation laser power of 0.43 mW in their NDSS-based photoresist (described in [20]).

5.5 3D writing

Most work is done on 2D structures attached to some kind of substrate. 2D structures benefit from the fast reaction and nucleation kinetics at the substrate interface. Furthermore, metallic structures via van der Waals forces usually attach well to the surface and tend to show a low surface roughness. Contrary, 3D structuring is impossible if particle diffusion and convection is faster than particle nucleation and growth. For example, Figure 7A shows an example where particles are locally created in the volume by a photoinitiated process but convection prevents their attachment to the line written on the substrate surface.

Three methods to tackle this challenge are found in the literature. First of all, slow writing speeds as shown by

Figure 7: 3D metallic structures.

(A) Convection and diffusion of particles is faster than their adsorption to an existing structure preventing structuring in 3D. Meanwhile, well-defined lines are fabricated on the surface of the substrate. (B) Examples of 3D metallic structures created within a host polymer matrix. Reprinted with permission from Refs. [88, 89, 95]. Copyright 2000, 2002, and 2008, Advanced Materials, Advanced Material, and Optics Express, respectively. (C) Two examples of 3D structures where polymerization and reduction is performed simultaneously. Reprinted with permission from Refs. [21, 87]. Copyright 2016 and 2016, Advanced Materials and Ricky Wildman et al., respectively.

Ishikawa et al. allow for 3D structuring, possibly because a large number of particles are created and, statistically, a sufficient number remains in the vicinity to attach to the structure (see Figure 5A [19]). Another route followed is particle generation within a matrix that prevents particle movement. The matrix may be a solid porous network with the pores filled with the desired photoresist, which has been shown by a number of groups (silver in a porous SiO_2 network [88], silver in a polyvinylcarbazole polymer network [89], and silver in a PVP polymer matrix [95]; Figure 7B). The matrix may, however, also be created at the same time and by the same photon source by photopolymerization. This has been shown by, for example, Blasco et al. [21], where Irgacure 2959 was excited to form radicals that polymerized the acrylate-functionalized poly(ethylene glycol) and at the same time reduced the HAuCl_4 precursor. The following writing parameters have been used: excitation wavelength of 700 nm, repetition rate of 100 kHz, and scan speed of $2.5 \mu\text{m/s}$. Liu et al. [87] used the initiator Irgacure 369 to simultaneously polymerize pentaerythritol triacrylate and reduce $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with the aid of ruthenium(II) complexes at an excitation wavelength of 780 nm, a repetition rate of 80 MHz, and

a writing speed of $10,000 \mu\text{m/s}$ (Figure 7C). However, the resulting structures only contained isolated gold nanoparticles near the surface of the polymer line.

Note that 3D structures, which require focusing through already written features during fabrication, are not feasible in liquid resists as scattering of the excitation mode at these features prevents accurate structuring. However, in solid resists, a latent structure, similar to analogue photography, may be fabricated and in a subsequent step may be developed. For example, Wu et al. have shown this [88]: the latent structure was obtained within an SiO_2 porous matrix with the pores filled with a solution of AgNO_3 . A solvent exchange step with a solution of AgClO_4 leads to development of the latent image and a subsequent solvent exchange step to fixation.

5.6 Properties and applications of state-of-the-art structures

State-of-the-art 2D metallic structures fabricated by photoreduction have advanced to be feasible for nanophotonic applications. For example, Figure 8 shows split-ring

Figure 8: Silver split-ring resonator arrays.

Overview and close-up of silver split-ring resonator arrays with (A) arm lengths of $1.9\ \mu\text{m}$ and a separation of $3\ \mu\text{m}$ and (B) arm lengths of $0.8\ \mu\text{m}$ and separation of $1.5\ \mu\text{m}$.

resonator arrays fabricated in our group using silver chloride as precursor and trisodium citrate as initiator (wavelength $780\ \text{nm}$, repetition rate $80\ \text{MHz}$, and scan speed $1\ \mu\text{m/s}$). The reaction products of trisodium citrate hereby act as stabilizers for the silver particles. The structures

are reproducible and their quality is very high: compared to the gold structures presented in Figure 3, the silver structures here show a less pronounced proximity effect and have a very uniform structure height. Potentially, the high diffusivity of particles and molecules within the

Table 2: Results of some significant contributions to the field sorted by date.

Material	Writing parameters	Dim.	Min. width	Rel. cond.	Application
Ag-poly. [89]	82 MHz, fs, 730 nm, $25\ \mu\text{m/s}$	3D	$0.70\ \mu\text{m}$	$\approx 1/1000$ (incl. contact)	
Ag [96]	76 MHz, fs, 780 nm, 0.5, $80\ \mu\text{m/s}$	2D	$5.00\ \mu\text{m}$		2D opt. gratings
Ag [18]	80 MHz, fs, 800 nm, 1.42, $24\ \mu\text{m/s}$	3D	$0.70\ \mu\text{m}$	$\approx 1/3$	2D and 3D wires
Ag [95]	76 MHz, fs, 752 nm, 1.25, $50\ \mu\text{m/s}$	3D	$0.20\ \mu\text{m}$	$\approx 1/22$	2D wires
Ag [20]	80 MHz, fs, 800 nm, 1.4, $2.5\ \mu\text{m/s}$	3D	$0.12\ \mu\text{m}$		2D opt. grating
Ag [85]	82 MHz, fs, 790 nm, 1.35	2.5D	$0.13\ \mu\text{m}$	$\approx 1/10$	2.5D wires, coil
Au [86]	80 MHz, fs, 780 nm, 1.45, $3\ \mu\text{m/s}$	2D	$0.23\ \mu\text{m}$	$\approx 1/7$	2D antennas, circuits
					2D coil, split-rings
Au-poly. [21]	100 kHz, fs, 700 nm, 1.4, $2.5\ \mu\text{m/s}$	3D	$1.00\ \mu\text{m}$	$\approx 1/20$	2D and 3D wires
Ag [94]	80 MHz, fs, 780 nm, 1.42, $1\ \mu\text{m/s}$, +cw	2D	$0.13\ \mu\text{m}$	$\approx 1/29$	2D wires on flex. substr.

Writing parameters, if given, are repetition rate, pulse duration regime, center wavelength, NA of focusing optic, and writing speed. +cw indicates that a second cw laser assists fabrication. 2D structures are fabricated on the substrate interface only; 2.5D indicates a substrate with a topology onto which the structures were written. Relative conductivity is compared to bulk conductivity of the respective pure metal.

water-based silver resist reduces the proximity effect. This silver resist therefore allows highly resolved structures to be fabricated. Especially, Figure 8B shows, to the best of our knowledge, the first example of silver structures fabricated by photoreduction that have a resolution of better than $1\ \mu\text{m}^{-1}$.

First steps have been made to extend this technology to the third dimension. Table 2 summarizes some significant contributions to the field. Obtained material and writing parameters are listed against obtained linewidths, structure dimensionality, and structure conductivity compared to bulk conductivity. Furthermore, we list if an application in photonics or electronics was shown. Although linewidths of state-of-the-art structures already scale down to little above 100 nm and conductivity is on the same order of magnitude as of the respective bulk material in 2D structures, the complexity of published 3D structures still seems to be limited.

6 Summary and outlook

Metallic microstructures spatially structured in three dimensions are essential for a large number of promising applications in electronics and photonics. DLW via photoreduction in principle provides almost arbitrary freedom of design and is thus a fabrication method well suited for rapid prototyping. However, the complex chemistry and physics involved makes this method challenging to control. This review gives an introduction into the underlying chemistry and physics of photoreduction and summarizes the routes taken by diverse groups to improve the quality and applicability of the thus obtained metal structures.

2D metallic structures fabricated via photoreduction have by now reached high quality. However, writing speeds are still low due to slow reaction kinetics. Further research into accelerators could lead to enhanced writing speeds. In addition, parallelization by multifoci may pave the way to high-throughput metal microstructure fabrication. The quality of 3D structures somewhat lags behind the quality of 2D structures. Some concepts, such as efficient photoinitiators, may be transferred from 2D structuring to 3D structuring. However, due to turbulences in the volume of water-based resists, 3D structuring requires additional research into host polymer matrices.

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