Academic Dissertation to be presented with the assent of the Faculty of Technology, University of Oulu, for public discussion in Kajaaninsali (Auditorium L 6), Linnanmaa, on May 10th, 2002, at 12 noon.
Kordás, Krisztián, Laser-assisted chemical liquid-phase deposition of metals for micro- and optoelectronics
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Oulu, Finland
2002

Abstract

The demands toward the development of simple and cost-effective fabrication methods of metallic structures with high lateral resolution on different substrates - applied in many fields of technology, such as in microelectronics, optoelectronics, micromechanics as well as in sensor and actuator applications - gave the idea to perform this research. Due to its simplicity, laser-assisted chemical liquid-phase deposition (LCLD) has been investigated and applied for the metallization of surfaces having practical importance (Si, GaAs, SiO₂, Si₃N₄, etc.) since the beginning of the 80s. By the invention of novel substrates (polyimide, porous silicon), it was adequate to work out new precursors or just adopt old ones and optimise LCLD in order to fabricate metallic micro-patterns upon these materials for various purposes.

According to the motivations mentioned above, LCLD was utilized for the fabrication of palladium (Pd) micro-patterns on polyimide (PI), polyimide/copper flexible printed circuit boards (PCBs), fused silica (SiO₂) and silicon (Si). The selective metallization of porous silicon (PS) has been carried out with nickel (Ni). Depending on the types of lasers, either the focusing (Ar⁺ laser beam) or diaphragm projection (KrF and XeCl excimer laser pulses) method was employed. In the course of the work, various precursors of the corresponding metals have been investigated and utilized.

In the beginning, the pyrolytic decomposition of palladium-amine complex ions ([Pd(NH₃)₄]²⁺) on PI by a scanned and focused Ar⁺ laser beam was optimised and discussed. Thick (up to several micrometers) and narrow (~ 10 µm) Pd conductor lines with electrical conductivity close to that of the bulk were obtained. In the continuation of these investigations, the precursor was developed further. [Pd(NH₃)₄]²⁺ was mixed with the solution of formaldehyde (HCHO) in order to induce the reduction of the metal complex ions. To our knowledge, we were the first - so far - who applied this solution and described the reaction. With the proper choice of the laser parameters, thin Pd films as catalyst layers for electroless copper plating were deposited utilizing Ar⁺ and excimer lasers as well. The chemically plated copper deposits - upon the obtained Pd film - have excellent electrical and good mechanical properties.

In the second part of the thesis, three practical applications (metallization of via holes drilled in PI/Cu flexible PCBs, end-mirror fabrication on single-mode optical fibers, and carbon nanotube growth on Pd activated Si and Si/SiO₂ substrates) of Pd LCLD were realized. The previously presented [Pd(NH₃)₄]²⁺ and [Pd(NH₃)₄]²⁺/HCHO precursors were employed for creating the catalyst Pd layers for the carbon nanotube chemical vapor-phase deposition and for the autocatalytic electroless chemical copper plating, respectively.

Finally, a simple novel method was introduced for the area-selective metallization of PS. Since the surface of PS reduces spontaneously most metals from their aqueous solutions, it is difficult to realize localized metal deposition from liquid-phase precursors on it. We proposed the application of a stable Ni plating bath from which the metal deposits only when the PS is irradiated with photons having wavelength shorter than 689 nm, thus making possible an area-selective laser-assisted metal deposition.

The deposited metal structures and patterns were analysed by field emission scanning electron microscopy (FESSEM) equipped with energy dispersive spectrometer (EDS), by the milling and imaging modes of a focused ion beam system (FIB), optical microscopy, profilometry, resistance, and by reflectance measurements.

Keywords: metallization, optical fiber, polyimide, porous silicon, printed circuit board
Acknowledgments

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I wish to thank my parents for the education, patience, regard, faith and devotion. Finally, my deepest gratitude goes to my wife Renáta Sebő, who always stood by and ministered to me during this adventurous and beautiful period of my life.

Oulu, March 2002

Krisztián Kordás
**List of abbreviations and symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AED</td>
<td>autocatalytic electroless deposition</td>
</tr>
<tr>
<td>CCVD</td>
<td>catalytic chemical vapor-phase deposition</td>
</tr>
<tr>
<td>CNT</td>
<td>carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor-phase deposition</td>
</tr>
<tr>
<td>EDS; EDX</td>
<td>energy dispersive spectroscopy; energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>FESEM</td>
<td>field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>FSD</td>
<td>focal spot diameter (at 1/e² intensity)</td>
</tr>
<tr>
<td>LCLD</td>
<td>laser-assisted chemical liquid-phase deposition</td>
</tr>
<tr>
<td>LCVD</td>
<td>laser-assisted chemical vapor-phase deposition</td>
</tr>
<tr>
<td>LIFT</td>
<td>laser-induced forward transfer</td>
</tr>
<tr>
<td>LPDS</td>
<td>laser-assisted pyrolytic decomposition of solids</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multi-walled carbon nanotube</td>
</tr>
<tr>
<td>N</td>
<td>number of laser pulses; scan number</td>
</tr>
<tr>
<td>P</td>
<td>laser power</td>
</tr>
<tr>
<td>PCB</td>
<td>printed circuit board</td>
</tr>
<tr>
<td>PI</td>
<td>polyimide</td>
</tr>
<tr>
<td>PLD</td>
<td>pulsed laser deposition</td>
</tr>
<tr>
<td>PS</td>
<td>porous silicon</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>vₛ</td>
<td>scan velocity</td>
</tr>
<tr>
<td>v&lt;sub&gt;growth&lt;/sub&gt;</td>
<td>growth rate</td>
</tr>
<tr>
<td>Φ</td>
<td>laser-beam fluence</td>
</tr>
</tbody>
</table>
List and summary of original papers

The thesis is based on the following eight papers, which will be cited in the text by their Roman numerals.


The research work presented in the thesis can be divided into three parts. The first part (Papers I-III) deals with palladium deposition techniques on polyimide (PI). In the second part, three different applications of the laser-assisted chemical liquid-phase deposition (LCLD) of Pd are presented (Papers IV-VI). The third part of the thesis is based on Papers VII-VIII, in which the manufacturing of porous silicon (PS) and the laser-assisted deposition of nickel thereon are introduced.

In the first study (Paper I), a method of metallic palladium (Pd) deposition on PI from aqueous ammonia complexed Pd\(^{2+}\) precursor \([\text{Pd(NH}_3]_4^{2+}\) was demonstrated by means of Ar\(^+\) laser direct writing. The effect of laser parameters – such as laser power (P), number of scans (N) and scan speed (\(v_s\)) – on the pyrolytic decomposition of the metal-complex, and hereby the deposition of Pd, were studied. It was found that by applying multi-scans (\(N > 4\)), scanning speeds of \(v_s \approx 100 \mu\text{m/s}\) and moderate laser power (\(P \approx 100 \text{ mW}\)), the deposited Pd patterns were thick (1-10 \(\mu\text{m}\)), bulky, continuous, homogeneous and adhesive, and their electrical resistivities were close to that of bulk Pd.

Paper II deals with a novel Pd seeding method on PI for consecutive electroless metal plating. The Ar\(^+\) laser-assisted deposition of Pd thin film was done utilizing the mixture of formaldehyde (HCOH) and \([\text{Pd(NH}_3]_4^{2+}\) precursor. The presence of HCOH ensured the reduction of \([\text{Pd(NH}_3]_4^{2+}\) and resulted in formation of thin Pd films (with thickness up to 50 nm) along the laser-scanning route of the polymer surface. Under optimal conditions, uniform metallic Pd patterns and – in a consecutive step of chemical electroless plating – Cu deposits can be generated on the top of PI with minimal feature size of a few micrometers.

The favourable properties of excimer pulses (fast, photolytic, large-area surface processing with high lateral resolution) gave the idea of Paper III, in which the previous experiments – done in Paper II – have been repeated by changing the focused beam of the Ar\(^+\) laser for projected pulses of KrF- and XeCl-excimer lasers. Parameters such as the number of pulses (N) and beam fluence (\(\Phi\)) were systematically varied and their effects on the formation of Pd films were studied. The correlation between the laser parameters and Pd formation was found to be strong, especially in the case of crystal growth rate as a function of \(\Phi\). The Pd layers deposited in this manner showed the same chemical activity for successive electroless metallization as was observed when the patterns were made with an Ar\(^+\) laser.

In Paper IV, a possible direct application of the aforementioned Pd thin film deposition is demonstrated. Via holes were drilled in PI/Cu flexible printed circuit boards (PCBs) by excimer laser-induced ablation and were activated (using the same method we described in Paper II) for chemical metal deposition in order to create electrical interconnects between the two sides of the PCBs. The developed method turned out to be useful in making conductive – both vertical and horizontal – interconnects.

The study in Paper V represents how the excimer laser-assisted Pd deposition can be adopted in a direct application. Thin Pd films were created on the core areas of single-mode optical fiber-ends (SiO\(_2\) doped with GeO\(_2\)) to achieve localized catalyst deposition.
for subsequent electroless copper plating. Such fabricated copper covers operate as end mirrors. The reflectivity of fiber-ends could be increased by up to 9 dB. The process was monitored through in situ optical measurements.

In Paper VI, tailored growth of individual carbon nanotubes and aligned nanotube networks on Pd activated Si and Si/SiO₂ surfaces are presented. The activation of Si and Si/SiO₂ substrates with Pd was realized by the laser-assisted thermal decomposition of [Pd(NH₃)₄]²⁺. The obtained surfaces proved to be suitable for catalytic chemical vapor-phase deposition of well-aligned multi-walled carbon nanotubes from ferrocene/xylene precursors.

Papers VII and VIII deal with the fabrication of Ni micro-patterns on porous silicon (PS) surfaces. The PS substrates – made by the anodization of boron (B) doped Si wafers – had been plunged into a commercial electroless plating bath of Ni and were illuminated using a focused and scanned Ar⁺ laser beam (VII) and projected KrF- and XeCl-excimer laser beams (VIII), respectively. Under laser exposure, thin, conductive and adhesive Ni films with thicknesses of several tens of nanometers were formed on top of the PS surface.

The basic ideas of the developed metallization techniques were the contribution of the author. The experiments were carried out in co-operation with co-authors mainly in the Microelectronics and Materials Physics Laboratories, Department of Electrical Engineering, University of Oulu, Finland. Some of the experiments were performed at the Department of Experimental Physics, University of Szeged, Hungary, at the Laser Laboratorium Göttingen, Germany and at the Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, USA. The analyses and measurements of the samples were executed by the author. The manuscripts for publications were written by the author – except Paper VI, in which the chapter dealing with the preparation of the catalyst was the author’s contribution – with the kind help of the co-authors.
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1 Introduction

1.1 Laser-assisted processing of materials

The discovery and construction of the first ruby lasers in the early 60s opened new routes in materials processing. Since that time, various lasers have been developed and, owing to the unique properties of laser light, lasers have become important in scientific research and industrial applications.

In the laser-assisted metal deposition techniques, lasers act as directed photon – as well as energy – sources providing a micro-reaction volume (or just simply, micro-reactor) by the illuminated zone [1]. Chemical reactions – on the substrate/surrounding media interface – occur because the absorbed laser photons cause a temperature increment near the interface and/or generate free radicals, excited electronic states or even free electrons, so that the irradiated areas can operate as catalytic active sites in the metallization. The focused laser beam can result in extraordinary high spatial intensities – especially in the case of pulsed lasers – and thus the system becomes far from the equilibrium, generating high temperature and concentration gradients in the interface region. This means that in some cases new reaction paths are open and chemical reactions take place, which could not happen in ordinary classical chemical systems close to the thermodynamic and reaction kinetic equilibrium [2].

So far, several laser-assisted direct processes have been established in order to fabricate metallic micro-patterns. The most frequently utilized techniques are laser-assisted chemical vapor-phase deposition (LCVD) [3-11], pulsed-laser deposition (PLD) [12-17], laser-induced forward transfer (LIFT) [18-25], laser-assisted pyrolytic decomposition of solids (LPDS) [26-31], and laser-assisted chemical liquid-phase deposition (LCLD) [32-55].

Most of the laser-associated metallization techniques cover a good range of metals that may be deposited on insulators and semiconductors, but their disadvantages are the necessity of vacuum and gas systems (LCVD, PLD), and dangerous compounds (LCVD). In the case of LPDS, the solid precursor (usually, metal-acetates and -acetylacetonates) is crystallized upon the substrate and decomposed by means of the scanned and focused laser beam. The basic idea of using liquid precursors and developing LCLD was to avoid
the use of the toxic precursors and vacuum technologies, as well as to avoid the pre-treatment steps like the spin-on coating of LPDS or the pre-metallization of the target by vacuum evaporation for LIFT. In addition, LCLD enables the creation of planar and 3-dimensional (3-D) microstructures by the means of additive methods without involving either masks or photoresists in the procedure (similarly to LCVD).

The topic of laser-induced metal deposition from solutions and liquid precursors has turned out to be an interesting research field with the advent of VLSI and ULSI microelectronics devices in the mid 80s. The need for small, micron-size metal features on the surface of microelectronics components – based on semiconductors (Si, GaAs, GaInP) and insulators (SiO₂, Al₂O₃, Si₃N₄, PET) – urged the development of novel and simple metallization methods for prototype applications and repairs of individual components. Although the related research fields were well-studied by the beginning of the 90s, further investigations were needed owing to the contemporary inventions and developments of novel substrate materials – having fascinating physical and chemical features – such as polyimides, composite polymers, porous silicon, etc.

In LCLD, all the substances needed for the metal deposition in the precursor (organic or inorganic metal compounds, chelating agents, pH-stabilizers (buffers), acids/alkalis, and reducing compounds) are dissolved either in distilled water or in organic solvents and contacted to the surface to be metallized. When the absorption of laser photons in solution is low at the wavelength of the operating laser, the solution of the metal-compound is spread upon the substrate, and the surface is illuminated through the liquid precursor layer (just like in our investigations). For low solution but high substrate transmittance, the substrate is used as a cover plate on the precursor, so the solution-substrate interface is exposed through the substrate.

The aforementioned advantages make LCLD an effective and promising tool for the fabrication of planar and 3-D metal structures on various substrates by additive means.

## 1.2 Principles of metallization

In this section, the background of both the classical chemical metal deposition and laser-assisted metallization methods of insulator substrates are introduced.

### 1.2.1 Classical chemical metallization methods using solutions

Classical chemical metallization methods, in which the goal is to create either metallic or alloy layers on the top of different non-conductive substrates, are mostly based on so-called autocatalytic electroless deposition (AED) reactions. These processes are autocatalytic because the deposited metal layer catalyses the reaction. The term “electroless” (or electrodeless) means that an external electrical-current source to provide electrons for reduction of metal-complexes is not needed because reducing agents mixed
into the precursor solution serve as electron donors in the reactions [2, 58-61]. Typical reactions are listed below:

\[
\text{Ni}^{2+} + \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{Ni} + \text{NaH}_2\text{PO}_3 + 2 \text{H}^+, \quad (1)
\]

\[
[\text{Cu(C}_4\text{H}_4\text{O}_6)_2]^{2-} + 2 \text{HCOH} + 4 \text{OH}^- \rightarrow \text{Cu} + 2 \left(\text{C}_4\text{H}_4\text{O}_6\right)^2- + \text{H}_2 + 2 \text{H}_2\text{O} + 2 \text{HCOO}^-, \quad (2)
\]

\[
[\text{Pd(C}_4\text{H}_4\text{O}_6)_2]^{2-} + \text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{Pd} + 2 \left(\text{C}_4\text{H}_4\text{O}_6\right)^2- + \text{NaH}_2\text{PO}_3 + 2 \text{H}^+. \quad (3)
\]

These reactions proceed only on surfaces with proper catalytic properties. Polymers usually do not show catalytic activity, and pre-treatment is necessary. A catalytic layer can be created on most surfaces (in a multi-step process of degreasing, etching, sensitising, etc.) depositing either Pd or Ag seeds/films [2, 36]

\[
\text{Pd}^{2+} + \text{Sn}^{2+} \rightarrow \text{Pd} + \text{Sn}^{4+}, \quad (4)
\]

\[
2 \left[\text{Ag(NH}_3\right)_2]^{+} + 2 \text{HCOH} + 4 \text{OH}^- \rightarrow 2 \text{Ag} + 4 \text{NH}_3 + \text{H}_2 + 2 \text{H}_2\text{O} + 2 \text{HCOO}^- . \quad (5)
\]

As soon as deposition of a metal seed occurs on the surface, there is no barrier for consecutive electroless metallization – by Reactions (1-3) – around the seed or on the catalyst film. It is worth noting that in microelectronics mainly Pd is used for this purpose because when biasing a conductor deposited on Ag catalyst undesired silver migration occurs along the wire.

Applying purely chemical methods, area-selective metallization of substrates is hardly possible. Since there is neither specified orientation nor self-assembly of the metal growth on the solid-liquid interface, deposition takes place all over the pre-treated and activated parts of the surface. When the goal is selective and localized metallization (including 3-D structures), other supplementary techniques besides plating have to be considered, such as lithography, laser processing, ion-etching, reactive ion-etching, etc. [2].

### 1.2.2 Laser-assisted chemical liquid-phase deposition (LCLD) of metals

The basic idea of laser-assisted metallization is that one can create a localized chemical reactor (at the interface of the illuminated surface and surrounding precursor) in which the metallization takes place on the desired parts of the substrate. Metallization is then localized and does not need masked photoresists, and many complicated steps of lithography may be skipped.

In general, the deposition mechanisms in LCLD are similar to those in LCVD. The difference is in the surrounding medium with different thermal and optical properties. The main steps of the mechanisms are [2]:

- Transport of reactant species (for electron change) from the far-away zone to the zone illuminated by laser light. The driving forces of the reactant flux are concentration and temperature gradients in the precursor medium.
- Reaction (decomposition, reduction, or oxidation of reactants) at the solid/liquid or solid/gas interface.
- Deposition of products and transport of side products toward the far-away zone.

In the course of laser-assisted liquid-phase deposition of metals, the laser beam can be considered as a (i) heat source (due to absorption and subsequent fast thermalization of the absorbed energy in both the liquid and polymeric media) and/or as a (ii) photon source (to liberate electrons, free radicals, etc. for the reduction of metal ions). In the former case, the processing is thermal (or pyrolytic) and the interacting photon energy is low (hv < 2 eV). The latter case (photolytic or photochemical mechanism) occurs when the energy of the laser photons is in the range of the chemical binding energies (2-5 eV). In both photolytic and thermal reaction pathways, the increment of laser power and pulse energy help to perform faster metallization of the polymer surfaces, but parallel to that, one has to consider several other effects cooperating in the process (diffusion limit of appropriate particles in the solution and on the surface of the substrate; bubble formation; convection in the liquid precursor, melting, re-solidification and/or ablation of the polymer; etc.).

In practice, neither pure thermal nor pure photolytic metallization processes can be found. Although both mechanisms take part in certain reactions, in most cases one of the types having specific dominance can be proposed.

In an ideal case (ignoring density changes, convective fluxes and also heat dissipation in the liquid), the thermally activated reactions are described through the heat flow equation [1]

\[
\frac{\partial \Delta H(x,t)}{\partial t} - \nabla \cdot [\kappa(x,t) \nabla T(x,t)] + \vec{v} \cdot \nabla \Delta H(x,t) = -\vec{k}_{I} \cdot I(x,t),
\]

where \( \Delta H \) is the total reaction enthalpy of the reaction, \( \kappa \) is the thermal conductivity, \( T(x,t) \) is the time-dependent temperature of a surface point at \( x \), \( \vec{v} \) is the scanning velocity of the laser beam, \( \vec{k}_{I} \) is the unit vector in the direction of the propagating light, and \( I \) is the effective intensity of the beam. In a real case, more terms (dealing with the heat dissipation into the liquid, thermal conductivity changes due to the deposited metal, etc.) have to be added to the left side of Eq. (6), thus making it rather difficult to find analytical solutions. The calculation of transport of the appropriate particles to the reaction zone is also complex in the liquid phase, because the convection, turbulence and bubble formation in the liquid can exceed the diffusion transport of species by several orders of magnitude. The contribution of these effects to the metal deposition results in different deposit morphologies and profiles (Gaussian, flat, volcano-like, and in some cases periodic structures) [1]. For thermal processes – because of the thermal conductivity of the substrate – the formed patterns are usually wider than the diameter of the laser spot. Moreover, when several laser scans are applied over the same pattern (in order to increase the thickness), the formally deposited metal – because of its good thermal conductivity – causes further increment in the width of the deposited patterns.
The general reaction kinetics for the thermal reactions is given by [1, 56]

\[ W(x,t) = A \cdot \exp\left(-\frac{\Delta E}{kT(x,t)}\right) \prod_i \Omega_i^{\Omega_i} X_i^{\Omega_i}, \]  

(7)

where \( W \) is the reaction rate, \( A \) is the pre-exponential Arrhenius parameter, \( \Delta E \) is the activation energy of the reaction, \( k \) is Boltzmann’s constant, \( T(x,t) \) is the time-dependent temperature of a surface point at \( x \), \( \Pi \) denotes the product over all types of species \( i \) to be reacted, \( X_i \) is the concentration of reactant \( i \), and \( \Omega_i \) is the partial reaction order for component \( i \). The exponential correlation between the reaction rate and the temperature gives reasonable explanation for the behavior of reactions at different temperatures during laser processing.

In photolytic laser processing, reaction rates are directly related to the number of excited or dissociated molecules in the reaction zone but not to the temperature of the system [1]:

\[ W(x,t)^* = k_0^* \prod_i \left[ n \sigma_i \left( \frac{I(x,t)}{h \nu} \right)^n \right] ^{\Omega_i} \prod_i X_i^{\Omega_i}, \]  

(8)

where \( W^* \) is the reaction rate, \( k_0^* \) is the rate constant, \( n \) is the number of the photons required for excitation, \( \sigma_i \) denotes the absorption cross section of component \( i \), \( I \) is the intensity of irradiation, \( h \) is Planck’s constant, \( \nu \) is the frequency, \( \Pi \) denotes product over all types of species \( i \) to be excited, \( X_i \) is the concentration of reactant \( i \), and \( \Omega_i \) is the partial reaction order for component \( i \). In a photolytic process, the thermal conductivity can be ignored since the reaction is a consequence of the interaction between the laser photons and matter. In other words, in a pure photochemical process, the reaction is limited to the areas illuminated by the laser, and thus the widening caused by the thermal diffusion on the precursor-substrate interface is minimal.

During the past two decades, numerous studies have been carried out in the field of LCLD. Deposition of most of the metals having technical and practical importance has been realized on numerous substrates. A summary of these investigations concerning the deposited metal, the substrate and the lasers (with their wavelength) used is given in Table 1.

In certain solutions, the metal to be deposited is not in an oxidized state. The metal is neutral but complexed with organic ligands (e.g., triphenyl phosphines, bisbenzenes). Since there is no need for reduction, the metal compound is only dissolved in a proper solvent (without any additive reducing agents) and decomposed by the incident laser beam, yielding metal deposition on the illuminated surface [40, 48]. The Ag\(^+\), Pd\(^{2+}\) and Pt\(^{2+}\) ammonia complexes decompose under thermal stimulation of a focused laser beam, resulting in the formation of metallic deposits [32, 33, I]. Other precursors follow reduction patterns found in normal chemical electroless plating, but the reaction is enhanced and localized in the focal volume of the laser [32, 35, 52, 53, I, II, IV-VII].
Table 1. A summary of experimental and theoretical studies of LCLD.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Substrate(s)</th>
<th>Laser (wavelength)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>PI</td>
<td>Ar' (488 nm)</td>
<td>40</td>
</tr>
<tr>
<td>Ag</td>
<td>SiO₂, Si₃N₄</td>
<td>Ar' (488 nm)</td>
<td>33</td>
</tr>
<tr>
<td>Al</td>
<td>Si</td>
<td>Ar' (488 nm)</td>
<td>34</td>
</tr>
<tr>
<td>Au</td>
<td>PI</td>
<td>2o Nd:YAG (532 nm)</td>
<td>35</td>
</tr>
<tr>
<td>Au-Ni plated Be-Cu</td>
<td>Ar' (488 nm)</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>Si</td>
<td>ArF (193 nm), KrF (248 nm)</td>
<td>37</td>
</tr>
<tr>
<td>Au</td>
<td>Si</td>
<td>Cu-vapor (514 nm)</td>
<td>38-40</td>
</tr>
<tr>
<td>Au</td>
<td>Si</td>
<td>HeNe (633 nm)</td>
<td>41</td>
</tr>
<tr>
<td>Au</td>
<td>SiC</td>
<td>ArF (193 nm), KrF (248 nm)</td>
<td>37</td>
</tr>
<tr>
<td>Au</td>
<td>SiC</td>
<td>2o Nd:YAG (532 nm)</td>
<td>35</td>
</tr>
<tr>
<td>Au</td>
<td>GaAs</td>
<td>Cu-vapor (514 nm)</td>
<td>38-40</td>
</tr>
<tr>
<td>Au</td>
<td>InP</td>
<td>excimer-pumped dye (580-720 nm)</td>
<td>42</td>
</tr>
<tr>
<td>Au</td>
<td>Al₂O₃</td>
<td>Cu-vapor (514 nm)</td>
<td>40</td>
</tr>
<tr>
<td>Au</td>
<td>TiO₂</td>
<td>Ar’ (354-364)</td>
<td>43</td>
</tr>
<tr>
<td>Cu</td>
<td>Si</td>
<td>Cu-vapor (514 nm)</td>
<td>38, 39</td>
</tr>
<tr>
<td>Cu</td>
<td>PI</td>
<td>2o Nd:YAG (532 nm)</td>
<td>35</td>
</tr>
<tr>
<td>Cu</td>
<td>PI</td>
<td>Ar’ (488 nm)</td>
<td>35, 40, 44, 45</td>
</tr>
<tr>
<td>Cu</td>
<td>Cr, Cu (on SiO₂, LiNbO₃)</td>
<td>Ar’ (488 nm)</td>
<td>46</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>KrF (248 nm)</td>
<td>47</td>
</tr>
<tr>
<td>Cr</td>
<td>SiO₂</td>
<td>Ar’ (488 nm)</td>
<td>48</td>
</tr>
<tr>
<td>Mo</td>
<td>W (on SiO₂)</td>
<td>Ar’ (514.5 nm)</td>
<td>49, 50</td>
</tr>
<tr>
<td>Mo</td>
<td>SiO₂</td>
<td>Ar’ (488 nm)</td>
<td>48</td>
</tr>
<tr>
<td>Ni</td>
<td>porous-Si</td>
<td>Ar’ (488 nm)</td>
<td>VII</td>
</tr>
<tr>
<td>Ni</td>
<td>porous-Si</td>
<td>XeCl (308 nm), KrF (248 nm)</td>
<td>VIII</td>
</tr>
<tr>
<td>Ni</td>
<td>InP</td>
<td>Ar’ (588-720 nm)</td>
<td>42</td>
</tr>
<tr>
<td>Ni</td>
<td>Mn-Zn ferrite</td>
<td>Ar’ (514.5 nm)</td>
<td>51</td>
</tr>
<tr>
<td>Pb</td>
<td>-</td>
<td>KrF (248 nm)</td>
<td>38</td>
</tr>
<tr>
<td>Pd</td>
<td>PI</td>
<td>Ar’ (488 nm)</td>
<td>32, I, II, IV</td>
</tr>
<tr>
<td>Pd</td>
<td>SiO₂</td>
<td>XeCl (308 nm)</td>
<td>V</td>
</tr>
<tr>
<td>Pd</td>
<td>PI</td>
<td>XeCl (308 nm), KrF (248 nm)</td>
<td>32, 52, 53, III</td>
</tr>
<tr>
<td>Pd</td>
<td>Si, SiO₂ (on Si)</td>
<td>Ar’ (488 nm)</td>
<td>VI</td>
</tr>
<tr>
<td>Pd</td>
<td>PET</td>
<td>XeCl (308 nm), KrF (248 nm)</td>
<td>32, III</td>
</tr>
<tr>
<td>Pd</td>
<td>SiO₂, Al₂O₃</td>
<td>Ar’ (488 nm)</td>
<td>33</td>
</tr>
<tr>
<td>Pd</td>
<td>Si, SiC</td>
<td>ArF (193 nm), KrF (248 nm)</td>
<td>38</td>
</tr>
<tr>
<td>Pt</td>
<td>SiO₂, Al₂O₃</td>
<td>Ar’ (488 nm)</td>
<td>33</td>
</tr>
<tr>
<td>Pt</td>
<td>InP, GaAs</td>
<td>excimer pumped dye (580-720 nm)</td>
<td>42</td>
</tr>
<tr>
<td>Pt</td>
<td>-</td>
<td>lamp 488 nm</td>
<td>54</td>
</tr>
<tr>
<td>Sn</td>
<td>TiO₂ (on glass)</td>
<td>Ar’ (514.5 nm)</td>
<td>55</td>
</tr>
</tbody>
</table>

For semiconductor substrates, there is no need for reducing agents, even if the precursor metal is in ionic form in the solution. The reduction and thus the metal
deposition takes place due to the local surface potential differences around the laser spot. The potential change caused by the charge separation is a consequence of the laser-assisted local heating [38, 39, 42, 51].

Basically two metallization processes can be distinguished. In direct metal deposition, the deposits have their final form ready for applications (electrical contacts and interconnections, optical masks, etc.). In the second process, the deposited films and seed layers serve as catalysts for further chemical treatments (e.g., AED, electroplating and catalytic chemical vapor-phase deposition) prior to real applications. The most frequently deposited catalyst for chemical plating of Ni and Cu is Pd. This method is used when the direct deposition of high-quality metal patterns with good electrical and mechanical properties is difficult, i.e., narrow, uniform copper patterns with high conductivity close to that of the bulk Cu has cannot be deposited directly on polyimide from the liquid-phase with present techniques. However, by depositing a thin Pd catalyst layer first, followed by treatment in an electroless copper bath, the desired high quality Cu patterns can be easily realized [32, 52, 53, II-V].

As seen above, the metal to be deposited has to be chosen to fit the application of interest. When good quality electrical conductors are desired, metals such as Al, Au, Cu, Pd and Pt provide the best performance. For catalytic purposes (for various chemical applications), usually Ag, Co, Fe, Ni, Pd and Pt are used. For magnetic applications, ferromagnetic metals (Fe, Ni, etc.) have to be selected, and so on.

1.2.3 Objectives and outlines of the thesis

The main target of the thesis was to study and develop area-selective metallization of various surfaces. Laser-assisted chemical liquid-phase deposition (LCLD) was used. LCLD techniques enable one to produce both planar and 3-dimensional metal patterns with high-resolution without optical and mechanical masks. Maskless methods are cost-effective and rather fast when certain micromodule components and individual prototypes are fabricated. Thus the objective was to work out the localized metallization of polyimide (PI), polyimide/copper flexible printed circuit board (PCB), silicon oxide (SiO₂), silicon (Si) and porous silicon (PS) by the LCLD of palladium (Pd) and nickel (Ni), respectively, for both basic [I-III, VII, VIII] and advanced [IV-VI] applications.

For PI, PI/Cu PCB, SiO₂, Si and Si/SiO₂ substrates, palladium was chosen because it can serve as a conductor and also as a catalyst material for further chemical treatments. We have optimised the laser-assisted decomposition of the known [Pd(NH₃)₄]²⁺ precursor on PI, Si, and Si/SiO₂ [I, VI]. By adding HCOH in the [Pd(NH₃)₄]²⁺ precursor solution, a novel Pd deposition method was developed and applied as well.

The selective metallization of PS – a material having fascinating properties – was also an objective of this thesis.
2 Experimental procedure

2.1 Substrates

Polyimide sheets (Kapton by Goodfellow) with thickness of 50 µm were used in Papers I, II, and IV. The metallization of via holes (work III) was carried out on flexible 75 µm thick copper clad polyimide PCB sheets (55 µm PI on 20 µm Cu foil). In all cases, the substrates were fixed to the sample holder. The surfaces to be metallized were gently cleaned with ethanol and dried prior processing.

The optical fibers – in Paper V – were made of SiO₂ doped with GeO₂ in the core. The diameters of the fiber and core were 125 µm and 9 µm, respectively. The fiber cleaving was done with a commercial tool (Sumitomo Electric, FC-P3).

Pristine and thermally oxidized Si (001) wafers (Si and Si/SiO₂, respectively) were used as substrates in Paper VI. The oxide layer thickness of Si/SiO₂ was ~ 100nm.

In Papers VII and VIII, the PS substrates were fabricated by the anodization of boron-doped (with resistivity of 0.015 Ωcm) Si (100) wafers in 5 M hydrofluoric acid, 13 M ethanol aqueous electrolyte. The current density (50 mA/cm²) and etching time (10-20 min) were monitored using a computer-controlled anodization cell. The cell was made of PVDF (polyvinylidene fluoride), and platinum was used as the cathode. The prepared PS samples were rinsed in ethanol and stored in pentane to avoid oxidation and cracking. According to the measurements performed in [57], the thickness and the porosity of the samples were 10-20 µm and 80%, respectively.

2.2 Precursors

The cleaned samples were submerged into reactive precursor solutions and the surfaces were illuminated through the thin liquid layer. Table 2 shows both the chemical composition and layer thickness of the precursors that were employed.
### Table 2. Solutions for laser-assisted metallization used in the thesis.

<table>
<thead>
<tr>
<th>Precursor Layer</th>
<th>Layer thickness</th>
<th>References (Metal/Substrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M PdCl₂, 1 M NH₃, 0.125 M NaOH</td>
<td>1 mm</td>
<td>I (Pd/PI), VI (Pd/Si; Pd/SiO₂/Si)</td>
</tr>
<tr>
<td>0.05 M PdCl₂, 2 M NH₃, 0.15 M NaOH, 6 M HCOH</td>
<td>0.2 mm</td>
<td>II (Pd/PI), IV (Pd/PCB)</td>
</tr>
<tr>
<td>0.005 M PdCl₂, 0.4 M NH₃, 0.015 M NaOH, 0.6 M HCOH</td>
<td>1 mm</td>
<td>III (Pd/PI)</td>
</tr>
<tr>
<td>0.007 M Pd(CH₃COO)₂, 0.3 M NH₃, 1.4 M HCOH</td>
<td>~0.5 mm</td>
<td>V (Pd/SiO₂)</td>
</tr>
<tr>
<td>Slotonip 30-1, electroless Ni bath</td>
<td>1 mm</td>
<td>VII, VIII (Ni/PS)</td>
</tr>
</tbody>
</table>

In Papers II and IV, the laser-deposited Pd patterns were subsequently plated by operating a commercial electroless copper bath, CUPRO-T-ECO (metal growth rate ~ 0.1 µm/min). In Papers III and V, homemade plating solutions (0.048 M CuSO₄, 0.24 M C₆H₅KNaO₆ (potassium sodium tartrate), 0.48 M NaOH, 1.48 M HCOH (formaldehyde), 3.9 M CH₃OH (methanol) and 0.014 M CuSO₄, 0.08 M C₆H₅KNaO₆, 0.1 M NaOH, 0.25 M HCOH, 0.7 M CH₃OH) were employed for the consecutive chemical metallization (with metal growth rates ~ 0.05 µm/min and 0.01 µm/min, respectively).

The samples were flushed in distilled water and dried with pressurized N₂ after each metallization procedures.

### 2.3 Lasers and optical configurations

A number of lasers were tried in the metallization process (Table 3). A continuous wave (cw) TEM₀₀ Ar⁺ laser was used in direct writing, and pulsed excimer lasers (KrF and XeCl) were used in projection patterning.

### Table 3. Parameters of the lasers utilized in the related metallization procedures.

<table>
<thead>
<tr>
<th>Laser (wavelength, duration, type)</th>
<th>Geometry</th>
<th>References (metal/substrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁺ (488 nm, cw, Spectra-Physics 171)</td>
<td>focused</td>
<td>I, II (Pd/PI), IV (Pd/PCB)</td>
</tr>
<tr>
<td>XeCl (308 nm, ~ 20 ns, ELI-94)</td>
<td>projected</td>
<td>VI (Pd/Si; Pd/SiO₂/Si), VII (Ni/PS)</td>
</tr>
<tr>
<td>XeCl (308 nm, ~ 20 ns, Lambda Physik EMG150)</td>
<td>projected</td>
<td>III (Pd/PI), VIII (Ni/PS)</td>
</tr>
<tr>
<td>KrF (248 nm, ~ 20 ns, Lambda Physik EMG150)</td>
<td>projected</td>
<td>III (Pd/PI)</td>
</tr>
<tr>
<td>dye-KrF hybrid (248 nm, ~ 500 fs, Szatmári-type)</td>
<td>projected</td>
<td>VIII (Ni/PS)</td>
</tr>
</tbody>
</table>

Laser beams were either focused (direct writing) or an illuminated diaphragm was projected (projection patterning) – through a thin precursor layer – onto the substrates to be metallized (Fig. 1). In the direct writing mode, the focused beam – with focal spot diameter (FSD) of ~ 3-4 µm at 1/ e² intensity – was scanned over the sample using a computer-controlled translation stage of mirrors and the focusing objective. The step and velocity accuracies were ~ 0.1 µm and ~ 1 µm/s, respectively. Both direct writing and
pattern projecting methods were monitored, projecting the image of the processed sample onto a CCD panel.

Figure 1. Beam propagations in the focusing (on the left) as well as the projective optical configurations (on the right). Note that the sample holders and thus the substrates are fixed. The lateral scanning is provided by the properly synchronized translation of both the mirrors and focusing microscope objectives.

2.4 Analyses and measurements

Profiles of the fabricated metal structures were investigated with a Dektak ST surface profiler. Images of the deposits were taken using optical microscopy (Olympus BH-2) (Papers II-VI) and scanning electron microscopy (Jeol JSM-6400F, Jeol JSM-6300F) (Papers I-III, VI-VIII). In Papers IV, VII and VIII, a focused ion beam device (FIB Micrion 2500 system) was also employed for preparing cross-sections and taking images.
of the samples. An accelerated Ga\textsuperscript{+} ion beam was focused and scanned over the surface of the sample. The collision of the ions with the sample caused ejection of atoms from the surface as well as the production of secondary electrons and ions. The former effect was used for etching or milling the sample of interest (high Ga\textsuperscript{+} ion dose); the latter was utilized for imaging by collecting either the emitted or backscattered charged particles (lower Ga\textsuperscript{+} ion dose).

The electrical measurements – either by the two- or four-point methods – were done with Fluke 8050A multimeters (with accuracy of \(\sim 5\%\)). A Wenthworth Probe Station was used for contacting the samples. \textit{In situ} reflectivity measurements – in Paper V –were performed using a standard fused-type 2×2 coupler (with 50\% coupling ratio by Sumicem) and a transmitter/receiver module (EXFO, FOT-50). The accuracies were \(\sim 20\%\) and \(\sim 10\%\) for signals below and over 1 dB, respectively. Chemical elemental analyses were carried out using energy dispersive spectrometers installed on both the Jeol JSM-6400F and Jeol JSM-6300F scanning electron microscopes.
3 Results and discussions

3.1 Pyrolytic decomposition of \([\text{Pd(NH}_3\text{)}_4]^{2+}\) complex

Aqueous Pd\(^{2+}\) ammonia complexes can be decomposed on Si\(_3\)N\(_4\) and SiO\(_2\) surfaces by using appropriate thermal agitation from Ar\(^+\) laser. Metallic palladium precipitation and release of various side products take place in the focal region. According to gas-chromatography measurements, the following chemical reaction has been proposed [25]:

\[
3[\text{Pd(NH}_3\text{)}_4]^{2+} \rightarrow 3\text{Pd} + 6\text{H}^+ + \text{N}_2 + 10\text{NH}_3 .
\]  

(9)

Paper I deals with palladium deposition optimised on PI. The aim of this study was to generate very fine, conductive and adhesive Pd structures on the substrate by tuning the experimental parameters, such as laser power (30-130 mW), scan speed (24-600 µm/s) and scan repetition (2-16 scans). The diameter of the focal spot was kept constant (FSD ~ 4 µm at 1/e\(^2\) intensity).

Figure 2. FESEM images of Pd structures on the PI surface. \(v_s = 200\ \mu\text{m/s}, P = 130\ \text{mW and FSD} \sim 4 \ \mu\text{m.} \ N = 2 \text{ and 4 scans in images (a) and (b), respectively. A high-magnification picture (c) shows the spongy Pd structure obtained after 4 scans [Paper I].}

During the first scans, the polymer surface became molten, and at the same time some metal was deposited along the pattern. Several scans were needed to form a continuous deposit. The metal patterns turn out to be formed of spongy palladium (Fig. 2). Increasing
the numbers of scans, the deposition took place already on the top of the sponge-like layer.

The scanning speed has a very important role in the formation of the deposits. Too fast scans ($v_s > 200 \, \mu m/s$) result in poor deposition, where the structure of Pd is porous (Fig. 3(a)). When the scanning velocity is reduced ($v_s > 100 \, \mu m/s$), the formed metal becomes compact and bulky (Fig. 3 (b)).

![Figure 3. Spongy (a) and bulk-like (b) Pd deposits on PI done using 130 mW of laser power, 16 scans, FSD ~ 4 µm and velocities (a) 300 µm/s and (b) 50 µm/s [Paper I].](image)

The proper laser power has to be chosen as well, in order to obtain deposition with good properties. Lower powers ($P < 70 \, mW$) give narrow and bulk-like Pd patterns without a spongy base material. At powers exceeding 70 mW, first sponge-like metal is formed, but later on – after several consecutive scans – the deposited layers become more and more compact, and finally bulky Pd is formed.

Figure 4 shows the measured resistances of Pd stripes (0.64 mm of length) deposited on PI as a function of scanning speed, laser power and scan number. Non-continuous – and thus non-conductive – structures were obtained after the first and second scan. After four scans, all stripes became conductive. The resistance values decreased with increasing number of scans. After more than from six to ten scans, the resistance values suddenly dropped. These decrements in resistance are very conspicuous at higher scanning speeds ($v_s > 300 \, \mu m/s$) – doubling the number of scans yields approximately a tenfold reduction in resistance. The resistance dependence is a non-monotonic function of the scanning speed. It has a local maximum at a speed of 60 $\mu m/s$ independent of the number of scans and laser power. For other speeds, the dependence is more or less monotonic. The slope is steeper at lower scan numbers than at higher ones. Low resistance and efficient metal-deposition at slow scanning speeds may be explained by a greater heating effect due to longer dwelling times of the beam.

Since the applied laser power determines the course of most laser-induced physical and chemical interactions, we also investigated the effect of this parameter on deposition. There was no significant metal deposition at powers below 30 mW. Palladium deposition started at 30 mW at low speeds ($v_s < 100 \, \mu m/s$) and high scan repetitions ($N > 8$ scans), and also at 40 mW at medium speeds (200–300 $\mu m/s$) and lower repetitions ($N < 8$ scans). It was found that the more power was applied, the better was the conductance achieved.
Figure 4. Resistance – vs. scan speed, laser power and scan repetition – of 0.64 mm long Pd stripes deposited on PI. The lowest resistivity values (~ 50 µΩ cm) were obtained when the parameters were as follows: \( v_s < 100 \mu m/s, \ N = 8-16 \) scans, and \( P = 90-130 \) mW [Paper I].

An explanation of this effect could be deduced from the thermodynamics as follows. When increasing the power, the temperature of the surface and solution (near the substrate) become higher. Dissociation of the complex is endothermic (\( \Delta H > 0 \)), and the direction of the chemical reaction is determined by changes in its Gibbs free enthalpy function [25]. The Gibbs free energy is defined as \( G = H - TS \). The change of Gibbs
energy of a chemical reaction at constant temperature is \( \Delta G = \Delta H - T \Delta S \), where \( \Delta H \) is the reaction enthalpy, \( T \) is temperature, and \( \Delta S \) is the entropy production of reaction. If \( \Delta G < 0 \), then the reaction is spontaneous. Because of decomposition and gas formation (see Eq. (6)), \( \Delta S > 0 \), so increasing the laser power at a high enough temperature, \( T \Delta S \) will be larger than \( \Delta H \), and \( \Delta G \) will be negative. This means that an increased laser power results in more efficient decomposition and formation of thicker Pd patterns with low resistance.

It is worth noting that in the same manner – namely by the decomposition of \([Ag(NH_3)_2]^+\) – silver (Ag) can be deposited on Si\(_3\)N\(_4\), SiO\(_2\) [25] and PI [32] surfaces. In the present study of palladium deposition, the applied laser powers (30-130 mW) were quite high – in order to provide the necessary heat for the thermal decomposition of \([Pd(NH_3)_4]^{2+}\) and thus the polymer suffered melting and slight deformation.

### 3.2 Reduction of \([Pd(NH_3)_4]^{2+}\) complex ions by HCOH

To avoid problems described above, applied laser powers had to be reduced. To ensure metallization at lower surface temperatures, the composition of the palladium-precursor \([Pd(NH_3)_4]^{2+}\) solution was modified by adding in formaldehyde (HCOH). The basic idea of this modification arose from the well-known Tollens test or “silver-mirror” reaction in which complexed Ag\(^+\) ions (e.g., by ammonia) are reduced by either proper sugars or formaldehyde, yielding a thin mirror-like formation of metal film on the wall of the test tube (see Eq. (5)). The reaction is rather fast – from a few seconds up to a minute, depending on the concentration of \([Ag(NH_3)_2]^+\) and HCOH in the solution. It cannot be used for laser direct writing because of the spontaneous metal deposition, but suggests that the addition of formaldehyde to \([Pd(NH_3)_4]^{2+}\) solution produces metallic palladium according to reaction

\[
[Pd(NH_3)_4]^{2+} + 4OH^- + 2HCOH \rightarrow Pd^0 + 4NH_3 + 2HCOO^- + 2H_2O + H_2. \quad (10)
\]

For \([Pd(NH_3)_4]^{2+}\) ions this reaction is very slow. Without agitation – even in a concentrated solution – it takes almost a day before a thin Pd film deposits on the wall of the container is obtained. Probably a poor deposition rate is the reason why the reaction has not been used before.

### 3.2.1 \(Ar^+\) laser-assisted Pd film deposition from the \([Pd(NH_3)_4]^{2+}/HCOH\) system

For laser-assisted deposition, this type of precursor is suitable because metallization can be localized and enhanced in the focal area of the laser beam. In Papers II-V, we used this solution for metallization purposes and did not encounter degrading/melting of the surfaces. During the processing, rather low laser powers were sufficient. As demonstrated in Fig. 5, no metallization took place under 10 mW of power (except when the scanning
speed was very slow, less than 100 \( \mu \text{m/s} \)). Using 5-15 mW at lower scanning speeds (\( v_s < 150 \mu \text{m/s} \)) and 10-20 mW laser power at faster scans (\( v_s > 150 \mu \text{m/s} \)), thin metallic Pd was formed. As soon as \( P > 25 \text{ mW} \), similar deposition occurred as was observed in Paper I under un-optimised circumstances.

![Figure 5. Types of palladium deposition (reactions) vs. laser power and scanning velocity (FSD ~ 4 \( \mu \text{m} \) at 1/e² intensity) [Paper II].](image)

Well-controlled thin Pd film formation described by Eq. (10) and under optimised conditions described by the mid-region in Fig. 5 was obtained. The advantageous laser parameters (low power, fast scanning) allow us to create narrow (~ 6-8 \( \mu \text{m} \)) and thin (< 50 nm) Pd patterns without destroying the PI substrate, thus providing an excellent catalyst for the subsequent electroless metal plating (Fig. 6).

In Fig. 6, both the catalytic thin Pd films (a, c) and copper deposits on these films (b, d) are seen. In patterns (a) and (c), the laser beam focusing parameters during the Pd deposition process were different. In tight focusing (when the focal plane of the processing laser beam coincides with the surface to be treated) the formed Pd layer is uneven. The thickness of the catalytic layer varies because \( \text{H}_2 \) bubbles – being released as long as the process is going on – hamper the beam and the deposition of Pd as well. This effect was avoided using defocused illumination in which more homogenous deposition took place because the formation of tiny bubbles could not shadow the whole section of the collimated beam. A drawback of defocusing is that the resolution of patterning decreases, where the width of Pd deposits increases up to 10-12 \( \mu \text{m} \).
Figure 6. Optical microscope images taken by an Olympus BH-2 microscope equipped with a CCD camera. Pictures (b) and (d) show the results of 5 minutes of electroless copper plating (CUPRO-T-ECO) on polyimide surfaces activated by the deposited palladium films (a) and (c) respectively. P = 20 mW, v_s = 300 µm/s, and N = 4 scans. When the Pd deposition is investigated by a focused beam (FSD ~ 4 µm) (a), the deposit is narrow but non-homogeneous. By defocusing the beam (FSD ~ 8 µm) (c), the unevenness decreases, but the width of the deposits increases [Paper II].

It is worth noting that repetition of scans along the same pattern yields more homogeneous and slightly thicker Pd films (up to 50 nm). The optimal number of scans was found to be 4-8. Increasing the number of scans could result in un-optimised decomposition of [Pd(NH₃)₄]²⁺, yielding a poor activation layer. The reason for this phenomenon is high optical attenuation of the beam in the pre-deposited Pd. The adsorbed photons – through thermalization – increase the surface temperature and promote thermal decomposition of [Pd(NH₃)₄]²⁺.

After 1-6 min of immersion in the Cu plating bath (CUPRO-T-ECO), the preliminary activated locations of the polymer sheet became covered with metallic bulk-like copper. The purity of the formed copper was high. No significant signs of other elements in the EDX spectrum were detected. The resistivity of the Cu coating was measured to be 2.1 ± 0.1 µΩ cm, which is only 23% higher than that of bulk copper has (1.71 µΩ cm). The growth rate of Cu was 1.4-1.8 nm/s under the conditions suggested by the company producing CUPRO-T-ECO. The adhesion of the formed copper deposits was excellent (> 20 MPa) as measured by peeling tests. When plating was carried out on palladium structures, which were deposited by using an unfocused laser beam, the edges of the copper deposits did not show as clear contrast as seen in the focused case (Fig. 6(a-d)). The patterns show a diffuse planar distribution as did the activator Pd layer, but the thicknesses of both the Pd and the Cu films remained constant.
It is suggested that Pd deposition is photochemical. Under normal circumstances where thermal agitation is used, the rate of Pd deposition is much lower than that in the laser-aided procedure. Observation of this phenomenon encouraged us to carry out similar experiments (viz. palladium deposition on PI from the same precursor \([\text{Pd(NH}_3\text{)}_4]^{2+}/\text{HCOH}\) with high-energy UV laser photons (XeCl, 308 nm ~ 4 eV and KrF, 249 nm ~ 5 eV).

### 3.2.2 Excimer laser-assisted Pd film deposition from the \([\text{Pd(NH}_3\text{)}_4]^{2+}/\text{HCOH}\) system

The optical configuration was modified compared to the procedure done with an Ar+ laser (see Fig. 1). A diaphragm was illuminated and projected onto the polymer to create a well-defined structure and to avoid ablation. Changes were also made in the precursor solution: the concentration of the \([\text{Pd(NH}_3\text{)}_4]^{2+}/\text{HCOH}\) solution was lowered (see Table II) because of the strong absorption of the complex in the UV.

After the first laser shot, a very thin (a few nanometers) and reflecting deposit layer was formed on the surface of the substrate. The film functioned as a kind of passivation film against the ablation of the polymer, thus allowing the application of laser fluences over the ablation threshold of PI. This shielding effect was significant. Considering the high reflection (54% at 308 nm and 47% at 248 nm) and high extinction (2.19 and 1.86 for the XeCl and KrF wavelengths, respectively) values of palladium [62], the latter beam interacted mainly with the already-deposited layer instead of the polymer. (It should be noted that the optical parameters given above are valid for bulk Pd, but due to the short wavelength of the irradiation, the formed Pd films could be approximated as bulk materials.)

![Figure 7](image)

**Figure 7.** Field emission scanning electron microscopy (FESEM) micrographs of different Pd structures on PI vs. pulse numbers. The deposition is performed with a XeCl laser at a fluence of 120 mJ/cm². Number of shots: (a) 50, (b) 200, (c) 2000. Image (a) shows a film-like layer of Pd with some tiny metal seeds. As can be seen in images (b) and (c), the growth of the metal layer continues until the small Pd crystallites cover the whole surface of PI [Paper III].

Figure 7 shows the evolution of the Pd film on PI vs. the number of the XeCl laser pulses. In the beginning (Fig. 7 (a)), a thin, non-homogeneous, filmy deposit was formed.
By continued illumination, the first crystallites appeared (Fig. 7(b)) and started to grow until they filled the lateral dimensions, forming a homogeneous, 2-300 nm thin conductive, metallic palladium film (Fig. 7(c)) on the polyimide surface. The characteristic Pd (111) peak (2Θ = 40.15° diffraction angle at the λ ≈ 0.1542 nm Kα-line of copper) was detected in the XRD pattern after 200 pulses (at fluence of 120 mJ/cm²) and 500 pulses (at 90 mJ/cm²).

The effect of beam fluence is much stronger than the influence of pulse repetition. Namely, a ~ 50% increase of the energy density enables one to reduce the number of laser shots to 1% of the original repetitions. According to Eq. (8), strong dependence of deposition growth on pulse energy becomes self-evident. Since the reduction of the palladium complex to metallic Pd requires two electrons, more photons are needed for the electronic state excitation in the electron donor molecules. This corresponds to a reaction generated with sequential photon-induced excitations and results in a non-linear correlation (some kind of power function) between the deposition rate and beam intensity.

When the KrF laser was applied for the process, the deposition behavior was slightly different. A filmy layer was formed – like in the XeCl laser-assisted deposition – but the development and growth of crystals were not observed. The element analysis, executed by EDX spectroscopy, showed Pd deposition with KrF excimer pulses under the same parameters as for XeCl, but ~3 times less palladium on the PI surface was detected. In spite of the poorer palladium formation on the surfaces with KrF radiation, the pre-treated substrates were appropriate for electroless copper plating (Fig. 8).

![Figure 8. Optical pictures of (a) pre-metallized PI (200 KrF-laser pulses at fluence 120 mJ/cm²) and (b) chemically-deposited copper on the pre-metallized substrate (plating time of 5 min in a bath of 0.048 M CuSO₄, 0.24 M KNa-tartrate, 0.48 M NaOH, 1.48 M formaldehyde, 3.9 M methanol) [Paper III].](image)

The results of the excimer laser-induced deposition were in keeping with those we obtained using an Ar⁺ laser in Paper I. The predicted and realized metal formation on the PI surface from [Pd(NH₃)₄]²⁺/HCOH by UV photons affirmed our previous assumptions in which a photolytic reaction mechanism was suggested. For further confirmation, a control experiment was carried out: the solution was heated up to 60 °C together with a piece of PI sheet in a test-tube. After a few minutes agitation, dark colloidal precipitation (Pd and PdO) was observed in the liquid media but not on the polymer. Unlike in the case of the laser-assisted process, a gray, mirror-like, metallic thin film of palladium was
formed on the substrate within the short dwelling times of both the Ar\(^+\) laser beam and excimer laser pulses.

Since the atoms and/or small clusters of noble metals (Pd, Au, Ag) do not form chemical bonds with the PI – but a weak dipole-induced dipole (with 5-10 kJ/mol binding energy) interaction is generated at the carbonyl group in the pyromellitimide unit of the PI [63] – only physisorption takes place. Basically, two kinds of interactions for the deposition mechanisms can be considered. One way, as was previously published in analogous work [52, 53], is that high-energy (4 eV for XeCl and 5 eV for the KrF laser) photons generate electron-hole pairs in PI near the polymer/solution interface, providing electrons to the metal ions for reduction, while the reducing agents (electron donors) in the liquid-precursor give their electrons to the surface. Another interpretation, according to surface catalysed heterogeneous reactions, is that the reacting parts (palladium-amine complex and formaldehyde molecules) are first adsorbed physically on the surface and have chemical interactions, thereby later to the attached metal deposition on the substrate takes place.

### 3.3 Applications of Pd LCLD

The simplest direct applications of palladium LCLD are direct writing of conductor lines and catalyst films on the polymer. Besides these purposes, the procedure is suitable for more specialised tasks. Here we introduce three sophisticated techniques dealing with the laser-assisted metallization: (i) via holes drilled in flexible PI/Cu (polyimide/copper) printed circuit boards (PCBs), (ii) metallic end-mirror fabrication on single-mode optical fibers, and (iii) catalyst preparation (Pd/Si and Pd/SiO\(_2\)/Si) for catalytic chemical vapor-phase deposition (CCVD) of carbon nanotubes (CNTs).

#### 3.3.1 Metallization of PI/Cu PCBs

The continuously decreasing dimensions in the microelectronics packaging industry have forced designers and manufacturers to look for and develop novel methods for creation of more compact PCBs [64-69]. Here, an alternative way – in which lasers are involved for the preparation of small metallized via holes – is presented [Paper IV].

Via holes were drilled in PI/Cu flexible PCBs using KrF excimer pulses (FWHM ~ 500 fs, \(\lambda = 248\) nm, fluence ~ 2 J/cm\(^2\)) in a diaphragm projection setup (for details, see Paper IV), and then pre-metallized using a focused (~ 4 µm in 1/e\(^2\) diameter) and scanned Ar\(^+\) laser beam (\(v_s = 20-800\) µm/s, \(P = 10-50\) mW and \(N = 1-20\)) (Fig. 9).
Figure 9. Schematic illustration of the Pd deposition. The drilled PCB material is fixed under a thin layer (200 µm) of [Pd(NH$_3$)$_4$]$_2^+/HCOH$ precursor [Paper IV].

In the pre-metallization step, a thin (20-50 nm) and narrow (2-10 µm) palladium layer was deposited on the polyimide-covered side of the PCB and on the wall of via holes using the laser-induced chemical liquid-phase deposition method. After the pre-treatment, the Pd covered holes were immersed into a Cu electroless plating bath to create the final copper interconnects (both vertically in the hole and horizontally on the PI) (Fig. 10).

As studied earlier, the growth rate of palladium film on the surface of polyimide depends on both the laser beam and solution parameters. In this work, the power of the incident beam, scanning speed and number of repeated scans were varied. Increasing the scanning speed of the beam over the surface resulted in poor palladium deposition. Therefore, repeated scans were required to obtain a continuous and regular Pd film deposition. Using a 15-25 mW laser power, with a 150-300 µm/s scanning speed and 4-8 scan repetitions, proved to be suitable for generation of a Pd layer sufficient for further electroless plating of copper (see Fig. 10). By using powers less than 10 mW, the Pd did not form. When the power was increased to over 30 mW, the palladium-amine complex molecules decomposed on the polymer surface due to increased local surface temperature, yielding thick (~ 1 µm) sponge-like palladium deposits and, at some places, degraded the PCB material. The Pd layer formed by the thermal-decomposition of the metal-complex is not a favourable catalyst for the production of narrow and regular electroless copper deposits.
The incident beam is not orthogonal to the surface (the angle of incidence is approximately 15° as seen in Fig. 10) when it passes through the cone-like via, and deposition of Pd is attained as well in the case of normal incidence to the surface. The formed Pd film is uniform over the entire surface inside of the via hole. This phenomenon is interpreted by taking account of the reflection of the laser beam on the wall of the via holes, which results in the illumination of the whole inner superficies.

After covering the via holes and desired interconnects with the palladium catalyst, the whole PCB was immersed into an electroless Cu plating solution. After a few seconds, a shiny and rather adhesive (> 20 MPa) copper formation was observed. The 2-5 min long plating time resulted in 0.2-0.5 µm thick copper deposits.

The resistivity of the copper was measured to be 2.2 µΩ cm, 25% greater than that of bulk copper. The resistance values of the metallized vias were ~ 10 Ω, much higher than...
expected. This anomalous high resistance can be due to poor contact between the original copper-covered side of the PCB and the chemically deposited copper layer. The formation of a non-conductive copper-hydroxide layer on the copper cladding during the palladium deposition process (due to the high pH > 13 of the solution) and/or the appearance of micro- and submicro-cracks in the metal coverage of the via holes can also play a role in this poor conductance. The exact cause requires further work such as chemical treatments before and after palladium deposition (flushing with acids to remove contaminations), as well as acoustic microscopy measurements regarding the detection of delamination between the original and deposited copper layers and cracks in the metal deposits.

### 3.3.2 Reflective metal coating fabrication on optical fibers

In this section [Paper V], the substrate to be metallized is not polyimide but fused silica (doped with GaO2). However, the process is analogous to the previous methods as presented in Paper III.

Optical fibers equipped either with internal or end mirrors play an important role in many applications of optoelectronics. A variety of methods – such as sol-gel, sputtering, lithography, vacuum evaporation – are known to be suitable for preparation of such metallic (Ag, Al, Cu) and dielectric (TiO2) reflective coatings [70-73]. Though these methods produce films of good quality, there is a drawback: when the reflective layer is desired only on the core of the fiber, one has to use masks in order to avoid coverage at the rest of the surfaces of the fiber.

In our approach difficulties arising from masking are eliminated. Firstly, a catalyst Pd thin film is locally deposited on the core of the fiber-section under controlled laser-aided chemical reaction in which the palladium-amine complex ions are reduced by formaldehyde (see Eq. (10)). Secondly, the Pd-covered core is chemically plated with Cu by autocatalytic electroless deposition (Reaction (2)). Since, the electroless copper plating takes place only on the catalytic sites of deposited Pd particles, formation of reflective copper mirror is limited to the treated areas of the fiber section (Fig. 11).

![Figure 11. Optical micrographs of optical fiber ends. Image (a) shows a Pd film covered core, which serves as a catalyst for the electroless copper plating (2000 shots, Φ ~ 0.5 J/cm²). In image (b), the same fiber is shown after 30 minutes of copper plating [Paper V].](image)
Depending on the laser fluence, usually 1000-5000 laser shots proved to be sufficient for appropriate Pd layer growth. The correlation between laser fluences and number of pulses used is a kind of inverse-proportional function. At moderated fluences ($\Phi < 0.5 \text{ J/cm}^2$), $N = 2000-5000$ pulses were needed, but when the fluence was increased ($\Phi > 0.5 \text{ J/cm}^2$), only 1000-2000 pulses were needed for catalytic treatment.

After the laser-assisted Pd deposition, the fiber end was immersed in a chemical copper plating solution. During the Cu growth, the reflectance of the fiber end was monitored at the working wavelength of the fiber (1350 nm). As seen in Fig. 12, the reflectance – first slightly then strongly – increases in time, and after 30 minutes it suddenly saturates, reaching the relative $\sim 9$ dB increase of reflectance. The origin was set at the reflection of the activated glass and Cu solution interface at the beginning of the plating.

![Figure 12. Temporal evolution of the optical reflectance on the fiber end (at 1350 nm) during electroless copper plating. As can be seen in the graph, the reflectance saturates after 30 min treatment [Paper V].](image)

### 3.3.3 Activation of Si and Si/SiO\textsubscript{2} surfaces for carbon nanotube growth

This section deals with the activation of Si and oxidized Si (Si/SiO\textsubscript{2}) substrates by using Pd seeding for subsequent chemical vapor-phase deposition of carbon nanotubes (CNTs). Although the topic is not related directly to concrete applications in micro- and optoelectronics, the advantageous physical properties of nanotubular structures (excellent thermal conductivity, metallic and semiconducting behavior, mechanical flexibility, etc.) give numerous possibilities to utilize the results – obtained in Paper VI – both in opto- and microelectronics [74-76].
Since the discovery of CNTs [77], the growth of both single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs, respectively) become a new and separated part of materials science. During the last ten years, methods such as arc-discharge, laser evaporation and catalytic chemical vapor-phase deposition (CCVD) have been developed and improved for the production of CNTs. Among the techniques mentioned above, only the CCVD of hydrocarbons proved to be useful for high-volume tailored synthesis. In CCVD, the nature and yield of the obtained nanotubes can be controlled by varying the parameters of the synthesis (the substrates, precursors and catalysts; the duration and temperature of the reaction; gas pressure, flow rate, etc.). Alumina (Al₂O₃), magnesia (MgO), silica (SiO₂) and various zeolites – the most frequently used substrates – are usually activated by Co, Fe and Ni [78-81].

Aligned or self-oriented growth of CNTs plays an advanced role in applications; therefore, one of the goals of the recent investigations is to find proper alternatives for such preparation methods [81-83]. In Paper VI, the results of the CCVD of highly-oriented MWCNTs – carried out on Pd activated Si and Si/SiO₂ substrates – are presented.

The catalyst Pd seeds were deposited on the substrates by the laser-assisted pyrolytic decomposition of [Pd(NH₃)₄]²⁺ (see Eq. (9)). The size of the obtained Pd seeds varied over the range 50-200 nm (Fig. 13 (a)). After the seeding process, the activated substrates were exposed to either methane (p_total ~ 100 Pa, T ~ 1000 °C, flow rate ~ 30 cm³/s in ~15 cm³/s Ar flow) or ferrocene/xylene (p_total ~ 50 Pa, T ~ 800 °C, flow rate ~ 30 cm³/s in ~15 cm³/s Ar flow). Depending upon the selected substrates and precursors, different structures were grown (Table V). Using methane as precursor, the growth was poor. CNTs were obtained only on Si/SiO₂ (thermally oxidized Si). In the case of a ferrocene/xylene mixture, deposition occurred on both Si and Si/SiO₂ substrates (Table 4).

<table>
<thead>
<tr>
<th>Substrate \ Precursor</th>
<th>Methane</th>
<th>Ferrocene/Xylene Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (001) SiC fibers</td>
<td>Medium-density layer of CNTs</td>
<td></td>
</tr>
<tr>
<td>Thermally grown SiO₂ (≈ 100 nm) on Si Separated individual CNTs covered with thick carbon layer</td>
<td>Well-aligned, high-density MWCNT layer (Fig. 13 (b))</td>
<td></td>
</tr>
</tbody>
</table>

Though numerous growth mechanisms of MWCNTs have already been proposed in the literature – such as the shell-by-shell growth, curling of graphite sheets and simultaneous growth of all shells – most of them are unconvincing. It is known that the catalytic syntheses of CNTs are strongly related to (i) the catalytic decomposition of carbon compounds on the catalyst metals, (ii) the formation of unstable carbides and (iii) the speed of carbon diffusion in the metal particle [81].
Figure 13. FESEM images of (a) Pd seeds on Si and (b) high-density MWCNTs deposited on Pd activated Si/SiO$_2$. The seeding was performed from the [Pd(NH$_3$)$_4$]$^{2+}$ precursor using focused (FSD ~ 3 µm) and scanned ($v_s = 50$ µm/s, $P = 0.6$ W) Ar$^+$ laser beam. The CCVD of MWCNTs were realized in a tube-furnace at 800 °C from ferrocene/xylene precursor [Paper VI].

3.4 Area-selective Ni deposition on porous silicon

The objective of this last section is localized metallization of porous silicon (PS). The unique physical and chemical properties of PS suggest it to be a promising material in micro- and nanotechnology related to optoelectronics [84-87], integrated devices based on Si [87, 88], sensor/actuator applications [89-92] and chemical catalysis [93-95] in the future. The applications mentioned usually require some kind of metal layers or metallic patterns on the top of the PS substrate (electrodes, contact masks, mechanical support, etc.). There are several different alternatives to make such metallizations, e.g., by lithography, but none of those methods is direct, meaning that a number of consecutive processing steps have to be involved including the applications of photoresist, masks, developing and other difficult steps.

Porous silicon, unlike polymers, ceramics and glasses, is a rather reactive material. In chemical reactions, PS acts as an electron donor reducing the surrounding media. This feature of PS causes difficulties when the goal is a metal structure with well-defined geometry on PS. Most of the metals having practical importance (Ag, Au, Fe, Pd, Pt, etc.) spontaneously deposit from their solutions onto the substrate as well as in the pores [96-99]. Therefore, the challenge is to find a stable precursor from which the metal ions cannot be reduced directly by the surface.

In our investigation, a commercial Ni plating bath (Slotonip 30-1) was used. The solution does not show chemical activity on PS without exposing the samples to the irradiation of proper photon sources.
3.4.1 Localized Ni deposition by focused Ar\(^+\) laser beam

The technical circumstances were similar to those we employed in other direct writing methods [32, I, II]. The samples were submerged in solution, and the focused laser beam was horizontally scanned along the surface. Already quite low laser powers resulted in the formation of Ni even at high scan velocities. The optimal parameters – when uniform, homogeneous and narrow Ni deposits form – were found as follows: \( P = 10-20 \text{ mW} \), \( v = 60-100 \mu\text{m/s} \) and \( N = 4-8 \) scans (Fig. 14).

The width of the deposited Ni lines did not change significantly on varying the parameters of the process (see the figures in Paper VI). A typical width of the written Ni deposits was 2-3 µm, which is equal to the diameter of the focused laser beam. The obtained resistivity values were ~ 10-15-fold higher (~ 100 µΩ cm) than that of bulk Ni (7 µΩ cm).

As was concluded from EDX analyses, the deposits contained ~ 10 atomic% of phosphorus and also 15 atomic% of oxygen impurities. Unfortunately, the chemical states of these elements could not be ascertained, but probably nickel-phosphorus alloys and nickel oxides caused the additive peaks in the EDX spectrum.

![Figure 14. FIB secondary electron image of a Ni line. The deposition was carried out with the following parameters: \( P = 10 \text{ mW} \), \( v = 60 \mu\text{m/s} \), FSD ~ 3 µm and \( N = 8 \) scans [Paper VII].](image)

To get a deeper insight to the metallization process, a control experiment was executed. PS samples were immersed into the Ni plating bath operated under optimal conditions. No deposition of Ni was detected even after five minutes exposure. It is worth noting that this experiment does not categorically preclude the possibility of a thermal process. For instance, it is known that some polymers can be metallized using the direct laser writing method in spite of the fact that they cannot be plated directly using conventional autocatalytic chemical procedures. To decide the initial step of the process, let us assume that, owing to the laser-induced heating, the surface of PS becomes catalytic and its temperature (at the focal spot) reaches the optimal value for the operation of the Ni plating bath (~ 90 °C). In this case, the deposition speed (growth rate) of Ni should be \( v_{\text{growth}} \sim 0.3 \mu\text{m/min} \) [100]. Considering the applied scanning velocities (\( v_s = 40-800 \mu\text{m/s} \)) and focal spot size (FSD ~ 3 µm) of the focused beam, the dwell time \( \tau \) can be calculated as \( \tau = \text{FSD}/v_s \), so \( \tau \) is approximately between 0.1 s (the slowest scan) and 0.005 s (the fastest scan), and thus the possible thickness of the formed Ni layer
(t = v_{\text{growth}} \tau) is between 0.5 nm and 0.025 nm. This range is notably less than the thickness of the patterns measured by profilometry and FIB. This means that the deposition process cannot be explained as a thermal electroless plating assisted by the focused laser beam. In all probability, the mechanism is photolytic rather than thermal. Namely, the absorption of laser photons in PS generates electronic excitations and emission of electrons [101, 102]. The Ni-complex molecules adsorbed on the surface are reduced, yielding metallic Ni deposits. The reducing agents in the plating bath provide electrons to the surface to fill in the electron loss of PS.

This model is not valid for consecutive scans because the beam cannot penetrate through the Ni layer deposited during the previous scans. In the second and subsequent scans, the character of the deposition changes for a thermal process. Although the nominal dwell time of the focal spot is still the same as in the first scan, the real dwell time increases owing to the good heat conductivity of Ni, yielding additional metallization along the connected Ni deposits far from the laser spot.

The constant width (independent of the laser parameters) of the deposited lines suggests a photolytic mechanism induced by the first laser scan. In further scans, poor heat conductivity of PS inhibits the heat flow in the substrate and yields a high temperature gradient along the PS surface perpendicular to the scanning direction. This results in a moderate surface temperature of the PS and exclusive metallization within the region of the previously deposited Ni.

The higher electrical resistivity of the patterns can be a result of formation of impurities in the metal during and after the deposition process. In the former case, the contamination arises from the plating bath in the form of Ni-P alloys, and in the latter case, the oxidation of Ni, which occurs due to the ambient air. Both impurities increase resistance. The effect of the morphology on the conductivity can also be significant. This is especially true for wires made by using only a few scans and for high scan speeds. Metallic overlap may not be perfect between the deposited layers.

### 3.4.2 Localized Ni deposition by projected excimer laser pulses

Since the prime Ni deposition mechanism on PS from the aforementioned precursor was supposed to be photolytic, it was plausible to perform further experiments using various photon sources. In Paper VIII, the investigations with lasers such as Q-switched Nd:YAG ($\lambda = 1064$ nm, $\tau = 150$ ns), Ti:sapphire ($\lambda = 745.5$ nm, $\tau = 120$ fs), XeCl excimer ($\lambda = 308$ nm, $\tau = 15$ ns) and KrF ($\lambda = 248$ nm, $\tau = 500$ fs) were carried out.

Experiments with Q-switched Nd:YAG and Ti:Sapphire lasers did not lead to deposition of Ni. Our observation is in keeping with the results of photoelectric measurements on c-Si/PS junction structures carried out in [102], where it was concluded that the photocurrent onset appears when the wavelength of the photoexcitation of the c-Si/PS junction is 689 nm. At wavelengths above this onset, very weak current signals were measured up to 950 nm, where it was cut off. In other words, considerable photocurrent of electrons as well as chemical reduction of Ni-complexes takes place when the wavelength of the excitation is shorter than 689 nm.

When XeCl laser pulses with pulse energies below the ablation threshold of PS were
used (under liquid, it was measured to be ~ 60 mJ/cm²), only a very thin Ni film is formed on the surface. The first laser shot produces a layer of metal with thickness of ~ 5 nm. The thickness of the deposit increases with the repetition of pulses and saturates at \( d_{\text{sat}} \approx 12 \) nm (\( N_{\text{sat}} \approx 10\text{-}15 \) shots). When the fluence exceeds the threshold value, two processes take place simultaneously: the first pulse removes the top of the surface (ablation), and in the meantime a thin primary Ni layer forms (laser-induced plating). For subsequent pulses, the Ni film acts as a filter, protecting the substrate from further ablation. After each successive pulse, because of absorption the incident fluence (on the PS/solution interface) decreases, resulting in lower and lower growth-per-pulse rate of Ni. Due to this negative feedback, the deposition tends to saturate, and the filling process of the shallow ablated hole stops. A cross-section image of such structure can be seen in Fig. 15.

![Cross-section image](image)

**Figure 15. Cross-section of the PS/Ni structure.** The preparation was done by the ion-milling mode of the FIB. The Ni film was generated using a XeCl laser with \( \Phi = 185 \text{ mJ/cm}^2 \) and \( N = 32 \) pulses. In the picture, the thin shiny layer deposited on the top of the porous silicon is Ni. The thickness is measured to be ~ 60 nm using a surface profiler. It is worth noting that due to the metallic top of the surface, the contrast of the image as well as the visibility of the pores improve [Paper VIII].

The ablation depth of the first laser shot, \( d_{\text{abl}} \), and the saturated thickness of the Ni deposit, \( d_{\text{sat}} \), increase with increasing laser fluence, \( \Phi \) (Table 5). The higher saturation-thickness of Ni for higher fluences is plausible if one takes into account that the absolute incident fluence (in PS, under the metal film) is what determines the deposition. Namely, the same fluence acts in the case of higher fluences when the layer of the absorbing metal is thicker.

**Table 5. Depth of ablation and maximal thickness of the metal layer vs. laser fluence [Paper VIII].**

<table>
<thead>
<tr>
<th>( \Phi ) (mJ/cm²)</th>
<th>( d_{\text{abl}} ) (nm)</th>
<th>( d_{\text{sat}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>110±15</td>
<td>60</td>
</tr>
<tr>
<td>123</td>
<td>35±5</td>
<td>20</td>
</tr>
<tr>
<td>77</td>
<td>25±5</td>
<td>15</td>
</tr>
<tr>
<td>60</td>
<td>0</td>
<td>12</td>
</tr>
</tbody>
</table>
The resistance values of the deposits were higher than expected. In the previous experiments, when the beam of the Ar+ laser was utilized for the metallization, the resistivity of the deposited Ni was measured to be ~100 µΩ cm. In experiments using excimer laser pulses, the resistivity of the formed metal proved to be much higher (~10^4 µΩ cm). The reason for the poor electrical quality of Ni can be associated with the precursor itself, since the plating solution was made for chemical plating but not for photochemical processing. (In order to create the best Ni layer, the solution should be heated up to 90 °C.) When an Ar+ laser was utilized, the thickness of the deposits did not show saturation in time, as concluded in [VII], and the metallization turned into conventional thermal chemical plating.

Experiments to obtain metallization using KrF femtosecond pulses (λ = 248 nm, τ ~ 500 fs) have been also carried out. Beside the advantageous properties of such laser pulses (focal spots with diameters in the sub-micron regime, short thermal diffusion length during the laser-matter interaction, etc.), there is a drawback in the conventional projective applications. Namely, the short pulse duration results in extremely high intensities, especially in the focal spot, where plasma formation in air occurs even at moderate pulse energies. As a consequence, the operations have to be carried out in vacuum. In order to avoid these difficulties, the beam was focused with a 350 mm focal length quartz lens, and the surface of the PS sample was positioned between the focal plane and the lens in order to prevent plasma-formation and breakdown in air. Because of undesirable optical effects like interference patterns, the proper analysis of these samples was not possible (see the optical image in Paper VIII). This problem was eliminated by using a Schwartzschild-type reflective objective. As the SEM image shows (Fig. 16), some micrometer size structures were deposited onto the surface of the sample using such an optical element.

Fig. 16. (a) Array of Ni spots on PS deposited from the liquid-phase precursor using a KrF femtosecond-laser. The pulses were focused by a Schwartzschild-type reflective objective in order to avoid the interference of the laser beam. (b) Higher magnification image of the Ni dot situated in the middle of picture (a) [Paper VIII].
In the present thesis, laser-assisted chemical liquid-phase deposition of metals on numerous substrates was studied. Both theoretical (mainly qualitative) and practical aspects of LCLD were investigated.

The Ar⁺ laser-induced pyrolytic decomposition of the $\text{[Pd(NH}_3\text{)}_4\text{]}^{2+}$ complex allowed the creation of Pd patterns with high lateral resolution (the minimal feature size was $\sim 10 \, \mu\text{m}$). Favourable electrical and good mechanical properties (resistivity of $\sim 50 \, \mu\Omega \text{ cm}$ and good adhesion, respectively) of the deposits suggest that the method is useful for applications.

In order to improve the performance of the metallization, the precursor was modified. By adding formaldehyde (HCOH) in the palladium ammonium complex solution, a novel precursor system ($\text{[Pd(NH}_3\text{)}_4\text{]}^{2+}/\text{HCOH}$) was obtained. With this reductive medium, the formation of thin Pd films along the irradiated parts of the PI surface could be realized. Compared to the pyrolytic decomposition of $\text{[Pd(NH}_3\text{)}_4\text{]}^{2+}$, only moderate laser powers were needed to reduce the metal, and very narrow (6-12 $\mu\text{m}$) and thin (< 50 nm) Pd deposits were obtained. The reduction of $\text{[Pd(NH}_3\text{)}_4\text{]}^{2+}$ by HCOH utilizing either Ar⁺ or excimer lasers is presumably a photochemical process rather than a thermal process. In a subsequent treatment, copper was plated on the Pd-covered parts of the substrate by autocatalytic electroless deposition (AED). The copper patterns showed excellent electrical (resistivity $\sim 2.1 \, \mu\Omega \text{ cm}$) and mechanical (adhesion $> 20 \, \text{MPa}$) properties. Diluted solutions of the same Pd precursor and KrF and XeCl excimer lasers were successfully used for deposition of thin Pd films for consecutive chemical copper plating.

It was also demonstrated that the developed Pd precursor enables Pd seeding for electroless Cu plating for special electrical (3-dimensional) and optical applications. Metallizations of via holes as well as optical fiber-ends were carried out. In the former case, both horizontal and vertical interconnects were created by using Ar⁺ laser-induced thin film deposition and chemical copper plating. The results are promising for applications where flexible PI/Cu PCBs are needed. In the latter process, Cu mirrors were obtained by AED of Cu on the Pd-seeding film, which was deposited prior to AED by excimer laser pulses utilizing the LCLD procedure. The proper relative reflectivity of the mirrors could be increased up to $\sim 9 \, \text{dB}$ by adjusting the plating time of AED.
Besides the aforementioned applications, the Pd deposits formed on Si and Si/SiO₂ surfaces were also suitable for the catalytic chemical vapor-phase deposition (CCVD) of aligned high-density multi-walled carbon nanotubes (MWCNTs).

The preparation and localized metallization of porous silicon (PS) were the last objectives of the thesis. The difficulties of selective metal deposition on PS from the liquid phase arise from the reactivity of PS. The spontaneous metallization of the samples was obtained by using a rather stable commercial electroless Ni plating bath. Deposition of Ni occurred only when the samples were irradiated with photons having wavelength shorter than 689 nm. Ni patterns with resolution of a few micrometers and with resistivity of ~15 times higher than that of bulk Ni were obtained when an Ar⁺ laser was used. Experiments executed with excimer lasers (KrF, XeCl) led to similar results, but the conductivity of the deposits was rather poor compared to the patterns created by the Ar⁺ laser. The mechanism of Ni deposition on PS has most probably a photochemical origin.

The presented basic investigations and their practical applications gave new results and contributions to previous studies in the field. In the thesis, the author emphasises the practical points of laser-assisted chemical liquid-phase deposition. Investigations concerning the modelling of temperature profiles of the laser-processed surfaces as well as chemical reaction kinetics/dynamics analyses will be performed during upcoming studies. In the future, further experiments will be executed to refine and utilize the developed techniques for other new applications (e.g., for sensors, actuators).
References


100. Slotonip 30-I operating datasheet (1996).
