Nano-scale patterning of aluminium films by water and light

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Table of Contents

Abstract ........................................................................................................ III

Kurzfassung ............................................................................................. V

Abbreviations ........................................................................................... VII

1 Introduction ........................................................................................... 1
  1.1 State of the art.................................................................................. 2
    1.1.1 Microlithography...................................................................... 2
    1.1.2 Nanolithography..................................................................... 3
  1.2 Innovation.......................................................................................... 5
  1.3 Overview of the thesis..................................................................... 6

2 Principle .................................................................................................. 7

3 Laser processing of planar aluminium films ............................................. 10
  3.1 Aluminium films on glass substrates ............................................ 10
    3.1.1 Experimental........................................................................... 10
    3.1.2 Results and discussion.......................................................... 11
    3.1.3 Computational thermal analysis......................................... 19
  3.2 Aluminium films on polymer substrates ....................................... 27
    3.2.1 Experimental........................................................................... 27
    3.2.2 Results and discussion.......................................................... 30
  3.3 Rapid prototyping............................................................................ 36

4 Subwavelength-sized aperture fabrication in aluminium by the use of an evanescent field ........................................ 39
  4.1 Introduction ...................................................................................... 39
  4.2 Experimental ................................................................................... 41
  4.3 Results and discussions.................................................................. 43
  4.4 SNOM experiment ......................................................................... 50
    4.4.1 Microscope set-up .................................................................... 50
    4.4.2 Measurements.......................................................................... 52
Abstract

Inexpensive patterning of metallic thin films on the micro- and nano-scale is of great importance for the fabrication of microelectromechanical systems. These metal films are commonly structured by an elucidated and time-consuming multi-step “lift-off” process requiring expensive clean-room facilities. Here, a novel, one-step lithography process for aluminium thin films based on low-power, laser-thermal corrosion in pure water is presented. Aluminium forms a thin passivating oxide layer when immersed into neutral water at room temperature. Heating of the metal film close to 100 °C due to absorption of the laser light provokes breakdown of this passivation. The aluminium corrodes and the reactants are washed away by the water. Crucial to this laser machining process is the confinement of heat production to a small volume in the metal film. This is achieved by, (i) using laser light of 488 nm or 532 nm wavelength, which is only absorbed by the metal film and not by the water, and, (ii) concentrating the light to a spot of limited spatial extent. The patterning set-up operates in common laboratory conditions and avoids the use of any acids or lyes that may damage other materials on the substrate.

In a first step, electrodes on planar substrates were fabricated by scanning a focused laser beam over an aluminium film and removing the metal by corrosion. Features sizing in the range of 270 nm to several micrometers in width were achieved in aluminium films on glass. The experimental results were successfully verified by a computational heat transfer analysis. The process required a power of only several milliwatts. This low-power property enabled the structuring of aluminium films on heat-sensitive materials such as polymers. Interdigitated microelectrode arrays have been fabricated on polydimethylsiloxane and SU-8 resist. By taking advantage of the inherent 3D device manufacturing capability of laser machining and SU-8 multilayered electrode structures were realised. Interconnections between the metal layers were fabricated by drilling holes through the SU-8 by laser ablation and subsequent metallization. Rapid prototyping and successful operation of a novel, asymmetric, two-phase electrohydrodynamic pump was demonstrated.

In a further step, subwavelength-sized patterning of aluminium films on pointed probes was realised by fabricating aperture probes for hybrid scanning nearfield optical and atomic force microscopy (SNOM/AFM) with high reproducibility. Aluminium corrosion on the scale below 100 nm was achieved by exposing the tip of an aluminium-coated AFM probe
made of silicon nitride directly to an optical evanescent field created at a glass-water interface by total internal reflection of a laser beam. Due to the irradiance decaying exponentially with increasing distance from the interface, only the aluminium at the front-most part of the probe tip was heated and corroded away. The tip was freed from the metal cladding up to a point where the nearfield radiation intensity fell below a certain threshold to induce corrosion. This self-terminating process yielded apertures of 38-115 nm diameter with silicon nitride tips protruding up to 72 nm. The height of these tips exhibited high reproducibility. Nearfield optical resolution in transmission mode of 85 nm was achieved on a high-contrast “topography-free” test sample.

Finally, aluminium films on planar glass substrates were structured in all three dimensions below the diffraction limit of light. A totally internally reflected laser beam at the glass-metal-water interface created an evanescent field on the aluminium film, which was locally enhanced by the tip of a scanning probe microscope. This intense nearfield below the probe tip enabled the patterning of 20-nm-thick aluminium films with holes of 40 nm diameter (aspect ratio of 1:2) and lines of 20-130 nm width.

In addition to the aluminium, the application of the laser-thermal oxidation process to other metals such as tungsten, silver, chromium, tantalum and titanium was investigated. Tungsten was successfully corroded, while the other materials allowed for surface oxidation.
Kurzfassung


wurde zudem zur schnellen Prototypenherstellung (Rapid Prototyping) einer neuartigen, asymmetrischen elektrohydrodynamischen Pumpe verwendet. Die mikrotechnische Struktur konnte erfolgreich getestet werden.


Neben Aluminium wurde das laserinduzierte Oxidationsverfahren auch für Metalle wie Wolfram, Silber, Chrom, Tantal und Titan untersucht. Wolfram liess sich erfolgreich korrodieren, während bei den anderen Materialien die Oberfläche lokal oxidiert werden konnte.
<table>
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<th>Abbreviation</th>
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
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<td>EBL</td>
<td>electron beam lithography</td>
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<td>EUV</td>
<td>extreme ultraviolet light</td>
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<td>FIB</td>
<td>focused ion beam</td>
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<td>IC</td>
<td>integrated circuit</td>
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<td>IEP</td>
<td>isoelectric point</td>
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<tr>
<td>MEMS</td>
<td>microelectromechanical system</td>
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<td>NA</td>
<td>numerical aperture</td>
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<td>NIR</td>
<td>near infrared</td>
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<td>PDMS</td>
<td>polydimethylsiloxane</td>
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<td>PMMA</td>
<td>polymethylmethacrylate</td>
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<td>RIE</td>
<td>reactive ion etching</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>SNOM</td>
<td>scanning nearfield optical microscopy</td>
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<td>SPL</td>
<td>scanning probe lithography</td>
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<td>SPM</td>
<td>scanning probe microscopy</td>
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<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>UHQ</td>
<td>ultrahigh-quality</td>
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<tr>
<td>UV</td>
<td>ultraviolet light</td>
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<td>VIS</td>
<td>visible light</td>
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1 Introduction

The fabrication of metallic structures is of great importance for the design of microelectromechanical systems (MEMS) employed in various fields such as micro-robotics (Jager et al., 2000), optical display technology (Dodabalapur et al., 1998), chemical sensing (Hagleitner et al., 2001) and biotechnology (Sanders & Manz, 2000). The applications of metallic features in such systems range from simple conduction of electrical currents for wires, to transport of electromagnetic signals in the MHz- and GHz-range for antennas, and to plasmonics at optical frequencies. The structure size varies between millimeters down to only several nanometers. Wires and bonding pads measure some tenths of a millimeter. Transistors for semiconductor devices on the contrary require features of less than one micrometer in width (Sze, 1985). Nanoelectronics demands for structure size in the order of 10 nm. The need for a wide range of structure size fostered the development of a variety of lithography schemes to meet the fabrication requirements in terms of resolution, throughput and costs. Fig. 1.1 provides an overview of lithography processes most commonly used today to fabricate features of 1 mm to 10 nm in size.

Fig. 1.1: Overview of common lithography processes.
1.1 State of the art

1.1.1 Microlithography

Patterning of metal films in the micro- and sub-micrometer domain is most commonly performed by a multi-step lift-off process (Sze, 1985). The substrate supporting the structured metal film is first coated with a thin layer of UV-sensitive, polymeric photoresist. The resist is then exposed to UV light through a chromium mask with transparent slits in the shape of the features to be transferred onto the substrate. Lenses below the mask can be used to reduce the pattern projected onto the resist, enabling structuring with feature sizes close to the diffraction limit of the light used. Currently light of 248 nm and 193 nm wavelength is used, allowing for a minimum structure size of 100-150 nm. In the future, IC manufacturers expect to change to light of 157 nm, pushing the resolution limit down to 80 nm.

After the UV exposure the photoresist is developed using chemical etchants, which remove the exposed or unexposed polymer and leave a structured resist film on the substrate. A thin metallic film is then deposited and subsequently lifted off by dissolving the resist, leaving a negative metal pattern on the substrate. Each process step is subject to defects introduced by dust particles and is thus performed in expensive cleanroom facilities. The process requires aggressive chemicals and involves costly lithographic masks. The masks are commercially available, however, their production can introduce unnecessary delays in the course of device developing and prototyping. In order to accelerate the fabrication process and to reduce cost and enhance flexibility, alternative parallel structuring schemes such as soft lithography (Xia & Whitesides, 1998) rapid photolithography (Qin, et al., 1996) and xerographic toner masking (Gleskova et al., 1995) were developed. This list can be extended by serial processes such as laser-chemical and -thermal processing (Bäuerle, 2000), and ink-jet printing (Szczech et al., 2002; Bieri et al., 2003). These fabrication schemes are especially suitable for microsystems of less demanding feature sizes than those needed in microelectronics. The resolution of rapid photolithography, xerographic masks and ink-jet printing is limited to several tens of micrometers. Soft lithography and laser machining on the contrary have proven to be successful tools for patterning in the micrometer range.

In recent years increasing attention was focused on polymeric microsystems such as plastic field effect transistors (Garnier et al., 1994), organic optical displays (Dodapalapur et al., 1998) and microfluidic systems (Sanders & Manz, 2000). Polymers such as polydimethylsiloxane (PDMS)
can be structured fast and inexpensively by micromoulding and offer three-dimensional device design by stacking individual layers (Jo et al., 2000). Moreover, polymers can exhibit good bio-compatibility, promoting novel devices for biomedical applications (Hyun et al., 2001). However, polymers show high sensitivity to heat and aggressive chemicals. Novel processes needed to be developed, which allowed for patterning of metal films on plastics in non-corrosive or even dry environment at low temperature. Microcutting (Stutzmann et al., 2000), cold-welding (Kim et al., 2000 and 2002) and nanotransfer printing (Loo et al., 2002) are some of the processes meeting these requirements. Like the previously mentioned soft lithography process, these fabrication schemes are based on physical interactions in the proximity of the substrate. They are unaffected by the diffraction limit of light and have thus great potential to advance the field towards nanolithography.

1.1.2 Nanolithography

The nanoscale fabrication of electronic structures is governed by two strategies known as the top-down and bottom-up approach. The bottom-up approach seeks ways to fabricate functional structures by assembling nanoscale particles and macromolecules. Single macromolecules integrated into conventional circuitry have been used to fabricate molecular electronics such as a C₆₀ amplifier (Joachim & Gimzewski, 1995) and a carbon nanotube channel transistor (Tans et al., 1998). Catenanes show promising application in molecular switches (Collier et al., 2000). The entropically driven assembly of molecules, so-called self-assembly, is an emerging technique to produce nanowires directly on the substrate (Lopinski et al., 2000; Chen et al., 2000). Self-assembly approaches permit rapid fabrication, but yet lack the ability to control growth location and shape, a property in great need for reliable connection of individual nanoelectronic features. Therefore, considerable effort is still invested in the top-down approach, in which concepts known from the macro- and microfabrication are downscaled for engineering on the nanoscale. By using extreme ultra-violet (EUV) light of 13 nm wavelength IC manufactures succeeded in fabricating structures of 20 nm width (Service, 2001). The short wavelength of the soft x-ray radiation reduces the diffraction limit towards the order of several nanometers enabling parallel farfield lithography in the range of tens of nanometers. A further decrease in the structure size is achieved by using electron beams of a “de Broglie” wavelength of about
0.01 nm. Lines of less than 5 nm are successfully fabricated in a thin layer of polymethylmethacrylate (PMMA) resist (Yasin et al., 2001). However, the high costs of the complex machinery employed by EUV and electron beam lithography (EBL) stimulated the development of alternative, inexpensive high-resolution processes, which rely on physical nearfield interactions to circumvent the diffraction limiting property of optical lithography. The use of light-coupling phase (Rogers et al., 1997) and amplitude (Schmid et al., 1998) contact masks enables the parallel fabrication of subwavelength-sized structures by exposing a resist to the optical nearfield. Processes such as soft lithography, micrcutting and nanotransfer printing already mentioned in the previous section, achieve nanoscale structuring by mechanical contact between a stamp and the substrate. However, these nearfield optical and mechanical lithography schemes require either a mask or stamp exhibiting nanoscale features of the same size than the desired structure on the substrate. Most often these masters are fabricated by conventional, expensive EBL. They are thus a convenient tool for fast and inexpensive replication. Direct, low-cost nanofabrication is currently dominated by scanning probe lithography (SPL). SPL was pioneered by Eigler and Schweizer (1990) by utilising a tip of a scanning tunneling microscope (STM) to move individual xenon atoms on a nickel surface and arrange them in the form of the letters “IBM”. These experiments initiated the development of a large variety of new SPL schemes to structure metal films on the nanometer scale. Atomic force microscope probes have been used for nanomechanical surface modifications such as indentation and carving of gold surfaces (Wendel et al., 1994). The scanning electrochemical microscope has been employed for electrochemical deposition of gold and silver in conducting polymer films and etching of copper thin films at high resolution (Hüßer et al., 1988). Moreover, STM tips made of gold served as solid-state field emission source for direct deposition of nanometer-sized gold structures (Mamin et al., 1990). Recently, anodic oxidation by STM and AFM gained increased attention for patterning metal films with electrically insulating or semiconducting metal oxides on titanium (Sugimura et al., 1993), chromium (Song et al., 1994), aluminium (Snow et al., 1996), niobium (Shirakashi et al., 1998) and molybdenum (Rolandi et al., 2002). Optical lithography below the diffraction limit of light has been realised by utilising scanning nearfield optical microscopy (SNOM) to expose a thin layer of photoresist (Wegschneider et al., 1995). The optical nearfield can also be used for direct photochemical vapour deposition of zinc on insulating substrates (Polonski et al., 1999).
In SPL the metal structuring occurs in the physical nearfield of the substrate to be patterned. The resolution therefore depends considerably on the area of interaction between the probe tip and the substrate, particularly on the size and shape of the probe tip. Common to all SPL techniques is the serial structuring property, which offers high flexibility in prototyping and development but is unsuitable for high throughput replication. A hybrid top-down and bottom-up process has recently been developed, which combines defined surface patterning by scanning probe microscopy (SPM) and rapid, parallel self-assembled growth of gold lines from suspension (Mesquida & Stemmer, 2002). The direction and shape of the line growth is pre-defined by an electrostatic template fabricated by SPL into a polymeric film.

1.2 Innovation

In this thesis a novel, one-step method for structuring aluminium films in the micro- and nanometer regime by direct, low power, laser-thermal corrosion in pure water on a set-up operating in common laboratory conditions is presented (Haefliger & Stemmer, 2002a). Aluminium thin films have previously been laser-machined by evaporation of the material, so-called metal ablation, or by chemical etching in gaseous (Koren et al., 1985) or liquid (Tsao & Ehrlich, 1983) environment. Combined photo-thermal and -chemical processing allowed for local oxidation of some metal films in air or controlled oxygen atmosphere (Wautelet, 1990). Laser oxidation of aluminium in air, however, proved to be self-destructive (Andrew et al., 1983).

In contrast to the above-mentioned methods, the laser-assisted corrosion process described here circumvents:

(i) any addition of acids, lyes and inhibitors to the liquid (Tsao & Ehrlich, 1983), which may corrode other materials on the substrate;
(ii) high laser power that may lead to thermal damage to underlying materials - a constant issue in laser ablation - and
(iii) expensive cleanroom and vacuum equipment.

Owing to the simple corrosion process and the flexible and inexpensive set-up, the new lithography scheme offers a convenient tool for rapid prototyping of lithographic masks and electrode structures for the devel-
opment of microelectromechanical systems. The structuring of the metal film is performed in one step, allowing for rapid fabrication without any delays introduced, e.g., by mask production. Since the substrate is submerged in water during structuring the susceptibility to pollution of the surface by dust particles is considerably reduced in comparison to lithography methods operating in air. The process therefore offers great potential for high yield production outside the cleanroom environment.

The low-power property of the lithography method makes it especially suitable for structuring aluminium films on heat-sensitive materials such as polymers (Haefliger et al., 2003b), addressing the increasing demand for "soft" structuring schemes to fabricate plastic MEMS. Since the process avoids aggressive chemicals it can also be considered as environment-friendly.

Direct machining of aluminium films on planar substrates by a focused laser beam enables the fabrication of sub-micrometer sized features with dimensions restricted by the diffraction limit of light. This physical limit can be surpassed by utilising nearfield optics. An evanescent field created by total internal reflection of a laser beam at a glass-water interface is used to remove aluminium from the tip of pointed probes on the nanometer scale (Haefliger & Stemmer, 2002b, 2002c and 2003). An intense, confined optical nearfield generated at the tip of an AFM probe allows for SPM-assisted corrosion of planar aluminium films on dimensions below 100 nm at a high aspect ratio of up to 1:2. In contrast to SPL procedures based on anodic oxidation the metal is removed in a single step, circumventing the need of a subsequent metal oxide etch process (Abadal et al., 1999; Rolandi et al., 2002). The scanning probe assisted corrosion process thus represents a convenient tool for nanoscale fabrication.

1.3 Overview of the thesis

The thesis is comprised of six main chapters. The first chapter provides theoretical aspects of the laser-thermal corrosion process. In the following three chapters selected applications of the corrosion process are demonstrated. With each chapter the resolution of the lithography method is increased in terms of lateral and vertical dimensions. Finally, the application of the corrosion process to materials other than aluminium is investigated and some conclusions are drawn.
2 Principle

Aluminium is known as a very reactive material which forms a thin passivation layer of hydrargillite ($\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$) when exposed to neutral water of pH = 7 at room temperature (Pourbaix, 1974). The aluminium is oxidised in an anodic reaction as follows (Fig. 2.1):

$$\text{Al} \leftrightarrow \text{Al}^{3+} + 3e^- \quad (2-1)$$

In the absence of any applied potential the sink for the electrons generated by the anodic oxidation (2-1) is the cathodic reaction, which occurs on the passive metal surface itself. In aqueous systems this reaction is generally the reduction of dissolved oxygen as:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \leftrightarrow 4\text{OH}^- \quad (2-2)$$

The overall reaction can thus be described as follows:

$$4\text{Al} + 6\text{H}_2\text{O} + 3\text{O}_2 \leftrightarrow 4\text{Al(OH)}_3 \quad (2-3)$$

The amorphous aluminium hydroxide $\text{Al(OH)}_3$ is not stable, but crystallises to give an electrically insulating layer of transparent monoclinic hydrargillite ($\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$).

\[ T = 25 \, ^\circ\text{C}, \, \text{pH} = 7 \]

*Fig. 2.1: Formation of passivating native oxide on aluminium immersed in neutral water at room temperature.*
Local heating of the material by absorption of laser light enhances the reaction rate of the oxidation process due to higher diffusivity of Al\(^{3+}\) ions through the oxide layer. Heat transfer from the metal film to the water also increases the diffusivity of oxygen molecules in the liquid and induces considerable convection that enhances oxygen supply into the reaction zone. Although the solubility of oxygen in hot water decreases, the higher diffusivity and convective flow is over-compensating for the oxygen depletion (Shreir et al., 1994). Moreover, the turbulence removes reactants like aluminium ions and hydroxide from the surface, leading to a steeper concentration gradient of Al\(^{3+}\) through the oxide layer, which stimulates the migration of aluminium ions to the reaction zone. The combination of these processes considerably increases the growth rate and thickness of the oxide layer on the aluminium film. At some point, however, high temperature in the substrate and water can inhibit passivation of the aluminium film and local corrosion occurs. In the case of high-level turbulence near the boiling point of water, the formation of hydroxide is partly inhibited since the aluminium ions are washed away and directly dissolved into the water. Apart from this fluid-dynamically-induced breakdown of passivation, thermodynamic calculations indicate:

(i) a significant increase of solubility of aluminium hydroxide and hydrargillite; and
(ii) a decrease of activation energy of reaction (2-1) with a simultaneous increase of activation energy of the reaction Al \(\rightarrow\) Al\(_2\)O\(_3\) at higher temperature (Shreir et al., 1994; Brook, 1972).

These phenomena can lead to a complete degeneration of the passive oxide film and to thermally induced corrosion of the aluminium in the laser-irradiated zone. This thermodynamically induced breakdown of passivation is illustrated in Fig. 2.2 by means of a phase diagram for the aluminium-water system at room temperature and 100 °C.

Photochemical contributions to the formation of aluminium oxide can be neglected due to the large energy band gap of about 8.3 eV of Al\(_2\)O\(_3\) (Palik, 1998), which is several times larger than the photon energy in the visible domain of light. For the following experiments, blue light of 488 nm (= 2.54 eV) and green light of 532 nm (= 2.33 eV) wavelength was used. Moreover, the light intensity required for this type of laser machining is too low to induce multiphoton processes.
Fig. 2.2: Phase diagram of the aluminium-water system at room temperature (solid lines) and 100 °C (dashed lines). The diagram is adopted from Brook (1972). If no electrical potential is applied to the aluminium, the metal is passivated at room temperature in neutral water of pH = 7 (black square). At elevated temperatures, however, the corrosion domains move towards lower pH driven by thermodynamic energetics. The pH of the neutral point shifts from 7.00 at 25 °C to 6.12 at 100 °C (white square). While at room temperature the neutral point lies within the passivation domain, it moves into the corrosion domain at temperatures close to the boiling point of water. The high chemical activity of the aluminium and the thermodynamically induced breakdown of passivation lead to a fast dissolution of the metal when it is heated close to 100 °C by laser light.
3 Laser processing of planar aluminium films

3.1 Aluminium films on glass substrates

3.1.1 Experimental

Thin aluminium films of 15-650 nm thickness were deposited by vacuum evaporation (BAE 120, Balzers) on microscope cover slips that were cleaned in air plasma prior to the coating. The patterning of the samples was performed on an inverted microscope (Zeiss Axiovert 100 TV) with an integrated, custom-made, piezoelectrically driven scan stage. A 100x/1.30-NA Plan-Neofluar oil immersion objective was used to concentrate the beam of a cw argon-ion laser (model 543-AP-A01, Melles Griot Laser Group, $\lambda = 488$ nm) to a spot of about 500 nm diameter onto the specimen (Fig. 3.1). The laser beam was coupled into the microscope objective by a mirror attached to the reflector block. A clean cover slip was placed onto the scan stage to serve as a support for the aluminium specimen. The sample was laid on the cover slip with the metal film facing the objective. Between the sample and the cover slip two spacers created a 15-$\mu$m-thin gap that was filled with ultrahigh-quality water (resistivity $> 18 \, \text{M}\Omega\text{/cm}, \text{UHQ}, \text{Elgastat MKII, Elga Ltd})$ by capillary forces. The thin water film provoked only small spherical aberrations of the laser beam and was completely transparent to light of 488 nm wavelength (Hale & Querry, 1973).

Fig. 3.1: Set-up for aluminium lithography on glass substrates (not to scale).
Fig. 3.2a-d: Laser induced oxidation of lines on a 100-nm-thick aluminium film. a,c AFM image (z-scale in a 130 nm, in c 110 nm). b,d Corresponding transmission light microscope image (objective: 100×/1.30-NA oil). Image size is 15 μm x 15 μm.

The laser light was thus absorbed by the aluminium only (skin depth at \( \lambda = 488 \text{ nm} \): 6.5 nm, Weaver \textit{et al.} (1981)), confining heat production to a small area on the metal film. After laser processing of the aluminium films, the structures were analysed by the inverted microscope in transmission mode and by an atomic force microscope (Topometrix Accurex II MS, ThermoMicroscopes).

3.1.2 Results and discussion

Scanning the metal substrate over the laser focus with a speed of several \( \mu \text{m/s} \) yielded either lines of electrically insulating hydrargillite due to enhanced passivation, or narrow grooves due to corrosion. The latter is expected if the temperature in the reaction zone approaches the boiling point
Fig. 3.3: Laser power limit for aluminium films of different thickness. The curve shows a linear behaviour for films of 15-70 nm thickness. Above 70 nm, saturation of the power limit is observed.

of water. This influence of temperature achieved in the reaction zone on the oxidation behaviour of the aluminium film during laser machining is illustrated in Fig. 3.2. Figure 3.2a,b shows corresponding AFM and light microscope images of two transparent lines of aluminium oxide in a 100-nm-thick film written at a speed of 1.8 μm/s and an incident laser power of 10 mW. In the AFM image (Fig. 3.2a), each optically transparent line of Fig. 3.2b appears as two 130-nm-high elevations separated by a 35-nm-deep depression. A comparison of the light intensity transmitted through the oxide lines (Fig. 3.2b) with the intensity transmitted through domains free of aluminium indicates complete through-oxidation. Figure 3.2c,d show structures on a 100-nm-thick aluminium film attained with a scan velocity of 1.9 μm/s and a higher laser power of 13 mW. This irradiation power was about 0.5 mW below the laser power that provoked boiling of the water by heat flow from the aluminium film. In contrast to the previous experiment the process now yielded 100-nm-deep grooves. Passivation of the metal film was partly inhibited and local corrosion of the aluminium occurred. These findings show good agreement with the theoretical predictions stated in chapter 2. Incident laser power above 13.5 mW caused local evaporation of the water and the formation of steam bubbles. The latter interrupted the oxygen supply to the metal surface and inhibited the cathodic reaction (2-2), resulting in an abrupt termination of the metal oxida-
Fig. 3.4a,b: Estimation of the temperature distribution in the aluminium film and glass substrate. a For thin metal films up to 70 nm thickness, the vertical temperature gradient in the aluminium is negligible. The heat flux in and out of the control volume in the metal film (dashed lines) is shown. The radius $w$ of the control volume corresponds to the radius of the laser spot. b For aluminium films thicker than 70 nm, the vertical temperature gradient in the metal film becomes significant.

Hence, an upper laser power limit exists, above which oxidation of the aluminium film in water becomes impossible. This limit is shown in Fig. 3.3 for aluminium films of different thickness. For thin films of 15-70 nm, the power limit increases linearly, which can be explained by the following estimation: The lateral temperature gradient in the metal film and the vertical gradient in the substrate by absorption of a focused laser beam is of the order of $\nabla T \approx \Delta T/ w$, where $\Delta T$ corresponds to the local temperature above ambient, $\nabla T$ the gradient of $\Delta T$, and $w$ is the radius of the laser beam at the surface (Bäuerle, 2000). Since the thermal conductivity of aluminium $\lambda_M$ is much higher than the conductivity of the glass substrate $\lambda_S$, any temperature gradient perpendicular to the metal film is neglected. The power absorbed in the illuminated area on the metal surface is:

$$ P_a = I_0 A \pi w^2, \quad (3-1) $$

where $I_0$ is the laser beam intensity at the surface, and $A$ the absorptivity (Fig. 3.4a). The heat transport from the aluminium film into the glass substrate is:

$$ \dot{Q}_s = \pi w^2 \lambda_s \nabla T \quad (3-2) $$
Fig. 3.5: Minimal achievable line width (solid curve) and corresponding scan velocity (dashed curve) for aluminium films of different thickness processed close to the laser power limit. The line width is defined by the full width at half-minimum of the oxidised trough.

and the lateral heat flux within the aluminium is:

\[
\dot{Q}_M = 2\pi w h \lambda_M \nabla T,
\]

where \( h \) is the metal-film thickness. The convective heat transfer into the water amounts to:

\[
\dot{Q}_C = \pi w^2 \alpha \Delta T,
\]

where \( \alpha \) is the heat transfer coefficient, which is assumed to be constant. In the case of stationary conditions,

\[
P_a = \dot{Q}_S + \dot{Q}_C + \dot{Q}_M = \pi w (\lambda_s + \alpha w) \Delta T + 2\pi \eta \lambda_m \Delta T.
\]

Assuming that boiling of water usually starts at a fixed temperature rise, \( \Delta T = \Delta T_B \), the incident laser power \( P_0 \), which is proportional to \( P_a \), shows linear dependency on the film thickness \( h \). For aluminium films thicker than 70 nm, the vertical temperature gradient in the metal becomes significant (Fig. 3.4b). Heat transport through the substrate and in a lateral direction close to the glass-metal interface becomes less efficient, leading to a saturation of the limit for thicker films. A more thorough analysis of the
Figs. 3.6: a) AFM image of lines of 266 ± 30 nm width in a 15-nm-thick aluminium film (laser power, 1.7 mW; scan speed, 25.5 μm/s). The image size is 10 μm x 10 μm, z-scale is 20 nm. b) Profile plot along the white line in a. c) AFM image of oxidised grooves of 460 ± 25 nm width in a 250-nm-thick aluminium film (laser power, 21 mW; scan speed, 0.57 μm/s). The image size is 10 μm x 10 μm, z-scale is 300 nm. d) Profile plot along the white line in c. Ridges on both sides of the groove indicate domains of aluminium oxide.

Temperature distribution in the laser-irradiated zone is demonstrated in section 3.1.3.

Figure 3.5 illustrates the minimal line width at half-minimum of the trough achieved with laser irradiation power close to the limit for aluminium films of different thickness. The width was measured by atomic force microscopy. The diagram also indicates the maximum scan velocity for permitting through-oxidation and dissolution of the metal film in the processed regions. The smallest line width of 266 ± 30 nm was achieved for a film of 15 nm thickness at a scan velocity of 25.5 μm/s (Fig. 3.6a,b). This corresponds to about \( \lambda/2 \) or the diffraction limit of the argon-ion laser light. Thicker specimens yielded broader grooves and a lower scan speed limit.
Fig. 3.7: Influence of lateral heat transfer on the oxidation process, measured for a 15 nm and 64-nm-thick aluminium film on glass.

(Fig. 3.6c,d). As shown in Fig. 3.6d, the laser-machined troughs were flanked by ridges of 20-50 nm height on both sides, representing domains of residual aluminium oxide.

Figure 3.7 demonstrates the influence of lateral heat transfer on the laser patterning process of aluminium films. For a certain metal film thickness, the line width increased with decreasing scan velocity. After through-oxidation and corrosion of the metal film in the laser focus, the light was absorbed by the glass substrate causing a temperature rise in adjacent areas due to heat transport in the glass substrate and the water film. This heating advanced the oxidation process away from the initial reaction zone. The lower the scan speed, the higher the total energy absorbed per unit line length and the further the heat diffused, both resulting in oxidation of a broader area. These effects allow direct writing of structures of variable width by adjusting the scan velocity. Since aluminium oxide is transparent to light in the optical regime, two-dimensional film patterning is possible without restrictions. When the laser focus meets regions already processed, the laser light can penetrate through the residual metal oxide and heat the adjacent metal film, promoting the oxidation away from the processed region. Figure 3.8 shows an image of the letters “HI” corroded into a 50-nm-thick aluminium film. The vertical lines were written at a speed of 1.4 \( \mu \text{m/s} \) and measure about 410 nm in width, the horizontal line inter-
Fig. 3.8: a Transmission light microscope image and b AFM image of the letters “HI” corroded into a 50-nm-thick aluminium film on glass. The images show an area of 16 µm x 16 µm. The vertical lines measure 410 ± 20 nm (scan speed, 1.4 µm/s), the horizontal line is 750 ± 20 nm wide (scan speed, 1.0 µm/s). The laser power was 9.5 mW. The lines are flanked by ridges of residual aluminium oxide.

secting two of the vertical troughs, was corroded at 1.0 µm/s and is about 750 nm wide.

The electrically insulating property of the aluminium oxide structures was verified by oxidising a line of about 500 nm width across the complete
waist of an X-shaped aluminium electrode of 100 nm thickness. The resistance between the ends of the electrodes increased from 16 Ω to more than 1 GΩ after processing, which corresponds to complete electrical insulation.

The structures presented so far were fabricated using the 100x/1.30-NA oil immersion objective. This objective provided features ranging between 270 nm and 600 nm at scan velocities close to the maximum speed at the laser power limit (Fig. 3.5). Broader lines were produced by reducing the writing speed (Fig. 3.7). However, to achieve lines wider than 1 μm, this approach turned rather inefficient since the time required to heat the area around the laser spot increased and led to a drastic decrease of the maximum possible writing speed. The fabrication of features larger than 1 μm was improved in terms of efficiency by the use of a bigger laser spot. This was achieved by applying objectives of lower NA. Table 3.1 gives an overview on some objectives and the performance investigated on a 30-nm-thick aluminium film on glass. The same set-up as described in section 3.1.1 was used for the experiments. For decreasing objective NA the minimum line width increased. In fact, the values of the minimum line width for the objectives investigated can be approximated by a curve proportional to Abbe’s law (Hecht, 1998), which determines the diffraction limited size of a focal spot from light projected by a lens:

\[ w_f = x \frac{\lambda}{2NA_{eff}}, \]  

(3-6)

where \( w_f \) denotes the line width, \( x \) a fitting parameter, \( \lambda \) the wavelength of the laser light and \( NA_{eff} \) the effective NA of the focused laser beam. Since the laser beam diameter is smaller than the back-aperture of the microscope objectives, \( NA_{eff} \) differs from the NA of the objective and is calculated as:

\[ NA_{eff} \approx n \frac{w_0}{f}, \]  

(3-7)

where \( n \) is the refractive index of the surrounding medium, \( w_0 \) the laser beam radius at the objective back-aperture and \( f \) the focal length of the objective lens. Good agreement between Eq. (3-6) and the measured data is achieved for \( x = 0.6 \). The fitting parameter mainly depends on the thickness of the aluminium film, which influences the minimum line width as demonstrated in Fig. 3.5.
<table>
<thead>
<tr>
<th>magn.</th>
<th>NA</th>
<th>laser power limit (mW)</th>
<th>min. line width (μm)</th>
<th>max. velocity (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>30</td>
<td>3</td>
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</tr>
<tr>
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<td>20</td>
<td>1.7</td>
<td>2.5</td>
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<td>0.75</td>
<td>5.2</td>
</tr>
<tr>
<td>100</td>
<td>1.30</td>
<td>3</td>
<td>0.36</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Tab. 3.1: Laser machining performance of various objectives on a 30-nm-thick aluminium film on glass.

Fig. 3.9: Line width attained with various objectives versus the effective numerical aperture $NA_{eff}$ of the focused laser beam. The values are approximated by a curve proportional to Abbe's law [Eq. (3-6)].

3.1.3 Computational thermal analysis

A numerical analysis of the temperature and heat flux in the aluminium film and the glass substrate was performed by a commercial finite element software (MARC/Mentat). The analysed system is illustrated in Fig. 3.10, showing the relevant section of the model and the appropriate boundary conditions. The model consists of axisymmetric, planar elements representing the aluminium film (elements in light grey) and the glass substrate (elements in dark grey). The analysis was performed for aluminium films of 28-650 nm thickness irradiated by a laser beam of 488 nm wavelength and about 460 nm in diameter. Owing to the small penetration depth of the blue laser light of 6.5 nm (Weaver et al., 1981) relative to the thickness of
the aluminium films considered, the laser light was assumed to be completely absorbed at the metal surface. The Gaussian laser beam profile (dashed curve in Fig. 3.10) was approximated by two coaxial beams of uniform intensity $I_0$ and $I_1$. $I_0$ corresponds to the maximum intensity of the Gaussian beam of a laser power of $P_0$. $I_1$ was calculated as:

$$I_1 = \frac{P_0 - I_0 w^2 \pi}{(w^2 - w_0^2) \pi}, \quad (3-8)$$

where $w_0$ corresponds to the diameter of the inner laser beam with uniform intensity $I_0$ and $w$ the diameter of the outer beam with uniform intensity $I_1$. $w_0$ equals the diameter of the original Gaussian laser beam. The absorbed laser power is then determined as $I_{a0} = AI_0$ and $I_{a1} = AI_1$, respectively (Fig. 3.10), with a theoretical absorptivity $A$ of the aluminium film in water calculated by means of the Fresnel coefficient, assuming that no light is transmitted through the metal film.
\[ A = 1 - \left( \frac{\sqrt{\varepsilon_M} - n_0}{\sqrt{\varepsilon_M} + n_0} \right)^2 \]  

(3-9)

where \( \varepsilon_M \) is the complex dielectric constant of aluminium and \( n_0 \) the dielectric constant of water. For light of 488 nm wavelength \( \varepsilon_M = -34.4 + i8.6 \) (Weaver et al., 1981) and \( n_0 = 1.33 \) resulting in \( A = 0.1 \). However, the surface roughness and the oxide covering the aluminium film can reduce the reflectivity of the metal and thus lead to enhanced absorption.

The thermal conductivity of bulk aluminium \( \lambda_M = 237 \) W/mK (CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1993). For submicrometer-thin metal films, however, grain boundaries can decrease this conductivity due to thermal contact resistances. For the glass substrate a thermal conductivity of \( \lambda_S = 1.11 \) W/mK was selected (datasheet for BK7 from Schott, Mainz, Germany).

Between the metal film and the substrate a perfect contact was assumed, leading to the following interface condition (Fig. 3.10):

\[ T_M = T_S \]

\[ -\lambda_M \frac{\partial T}{\partial z} = -\lambda_S \frac{\partial T}{\partial z} \]  

(3-10)

where \( T_M \) and \( T_S \) are the temperature at the interface in the aluminium and glass substrate, respectively, and \( z \) the axes perpendicular to the interface.

The heat transported from the aluminium surface into the water by free convection [Eq. (3-4)] was approximated by means of a film coefficient \( \alpha \) and the following boundary condition:

\[ -\lambda_M \frac{\partial T}{\partial z} = \alpha(T - T_0) \]  

(3-11)

where \( T_0 \) is the ambient temperature of the water. The film coefficient was assumed to \( \alpha = 100 \) W/m\(^2\)K. As experimental (Tuckerman & Pease, 1981) and computational (Weissberg et al., 1992) work showed, conventional laws for the calculation of the coefficient for free and forced convection (Holman, 1990) are in general only applicable to the macroscopic domain. To provide an estimation of the convective heat transfer in the present
problem, $\alpha$ was derived from measured heat transfer data of a micro cooling-channel network published in Haefliger et al. (2000). The ambient temperature was set to $T_0 = 25 \, ^\circ C$.

Finally, the axisymmetry of the calculated system was implemented by a boundary condition of the Neumann type applied to the element edges coinciding with the axis of rotation (Fig. 3.10):

$$\frac{\partial T}{\partial n} = 0,$$

(3-12)

where $n$ is the vector normal to the axes of rotation.

In the following, the system outlined above is used to calculate the laser power limit for aluminium films of different thickness. At the power limit the laser-illuminated metal is heated up just below 100 °C. The duration of this transient temperature increase is estimated by solving the differential equation in the control volume depicted in Fig. 3.4a:

$$m_M c_M \frac{\partial T}{\partial t} = P_a - \dot{Q}_S - \dot{Q}_M - \dot{Q}_C.$$  

(3-13)

where $m_M$ denotes the mass of the aluminium in the control volume and $c_M = 897 \, J/kgK$ (CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1993) the heat capacity of the metal. The absorbed laser power $P_a$ and heat flux $\dot{Q}_S$, $\dot{Q}_M$, and $\dot{Q}_C$ are described by Eq. (3-1), (3-2), (3-3) and (3-4) of section 3.1.2. The solution of the differential equation (3-13) is:

$$T = \left( T_0 - \frac{a}{b} \right) e^{-t/a} + \frac{a}{b},$$

(3-14)

with

$$a = \frac{m_M c_M}{\pi w^2 \alpha + \pi w \lambda_s + 2\pi h \lambda_M},$$

(3-15)

and

$$b = \frac{m_M c_M}{I_0 A \pi w^2 + (\pi w^2 \alpha + \pi w \lambda_s + 2\pi h \lambda_M)T_0},$$

(3-16)
where $T_0$ is the initial temperature of the aluminium film, substrate and water. For a 105-nm-thick metal film the time constant $a$ of the transient heat flux period is calculated to about 0.3 ns. The aluminium film is thus heated close to 100 °C within several nanoseconds upon laser illumination. By laser-drilling holes through a 105-nm-thick aluminium film a reaction rate of the oxidation of several 100 nm/s was observed. The oxidation thus occurs on a much slower time scale than the transient heat flux period of the metal film. Hence, after the aluminium film is heated to about 100 °C the metal removal by the corrosion remains insignificant for several milliseconds, in which the state of the system can be described as quasi-static. Exactly this quasi-static interval is most relevant to the calculation of the laser power limit. If the incident laser power exceeds the power limit the water over the aluminium film evaporates right after the aluminium film reached 100 °C, causing only minor corrosion of the metal. In the quasi-static interval the temperature and heat flow in the system can be analysed by the following Poisson equation:

$$\nabla^2 T + \frac{\dot{Q}^m}{\lambda} = 0,$$

(3-17)

where $\nabla^2$ denotes the Laplace operator and $\dot{Q}^m$ the energy flux produced per volume by the absorbed laser light. Due to the slow reaction rate of the metal corrosion any heat generated by the chemical process is negligible.

The dashed curve in Fig. 3.11 shows the calculated laser power limit for aluminium films of different thickness calculated by applying the bulk value for the thermal conductivity of the aluminium film ($\lambda_M = 237 \text{ W/mK}$). An absorptivity $A = 0.2$ provided good correlation between the simulated and measured data (Fig. 3.3) for films thinner than 100 nm. This absorptivity is larger than the calculated value [Eq. (3-9)], suggesting reduced reflectivity of the aluminium surface in water due to oxidation. The divergence of the calculated and measured laser power limit for aluminium layers thicker than 100 nm may originate from a deviation between the thermal conductivity of the actual aluminium film and the bulk value mentioned previously. The heat transport away from aluminium layers to the substrate becomes less efficient for thick films as outlined in Fig. 3.4b, rendering the heat conduction within the metal more relevant than for thin films. A smaller thermal conductivity of the aluminium would decrease the heat flux away from the laser-irradiated area, reducing the laser power limit. In fact, the repeated calculation of the laser power limit with
Fig. 3.11: Calculated and measured laser power limit. The measurement data was adopted from Fig. 3.3.

an average thermal conductivity for aluminium of $\lambda_M = 200 \text{ W/mK}$ and an absorptivity $A = 0.2$ shows excellent agreement with the measurement data (Fig. 3.11, solid curve). A maximum deviation of only 10 % to the measured values was achieved. The calculated laser power limit increases almost linearly for thin metal films as postulated in section 3.1.2 and saturates for thicker films. The reason for the saturation behaviour is explained in detail by Fig. 3.12, which illustrates the temperature distribution and relative heat flux in the section of the finite element model depicted in Fig. 3.10. For this calculation $A = 0.2$ and $\lambda_M = 200 \text{ W/mK}$. The relative heat flux is determined as:

$$q'' = \frac{\dot{Q}''}{P_L},$$

(3-18)

where $\dot{Q}''$ denotes the absolute heat flux in mW/μm² and $P_L$ the incident laser power. The relative heat flux simplifies the comparison of heat flow in models of different aluminium film thickness and laser power limit. For 40-nm-thick films no temperature gradient perpendicular to the metal surface is observed due to a large thermal conductivity of aluminium (Fig. 3.12a). The heat transport into the substrate is very efficient as demonstrated in Fig. 3.12b. However, for aluminium films of 105 and 220 nm thickness, a considerable temperature gradient below the laser-irradiated
Fig. 3.12: a,c,e Calculated temperature distribution and b,d,f relative heat flux in the section of the finite element model depicted in Fig. 3.10 for aluminium films of a,b 40 nm, c,d 105 nm and, e,f 220 nm thickness ($A = 0.2, \lambda_M = 200 \text{ W/mK}$).
area along the z-axis evolves (Fig. 3.12c,e), reducing the heat transfer to the substrate and in the lateral direction of the aluminium film close to the metal-glass interface (Fig. 3.12d,f). The saturation of the laser power limit is thus caused by a low efficiency in heat transport away from the laser-irradiated area. Figure 3.13 illustrates the temperature distribution along the z-axis of Fig. 3.12a,c,e, making the gradient in thick aluminium films perpendicular to the metal surface evident.

The temperature distribution and heat flux in the aluminium film and substrate illustrated in Fig. 3.12 show the situation at quasi-static conditions before the corrosion leads to a considerable removal of the metal. Although the heat in thin films (Fig. 3.12a,b) is transported farther away from the laser focus than for thicker films (Fig. 3.12e,f), experiments revealed the minimal achievable line width to be smaller for thinner films (Fig. 3.5). The line width thus seems to be influenced by the reaction rate of the corrosion process. Through-oxidation of thin films can be accomplished faster than for thicker films, allowing for a higher writing speed. An increased scan speed reduces the hot period of a fixed area on the aluminium film, limiting the advance of the corrosion away from the laser focus in lateral direction and leading to narrower lines in thin metal films.

In summary, the computational analysis presented in this section confirmed theoretical considerations performed in section 3.1.2 and provided
insight into the heat transfer in the laser-processed aluminium film and the substrate.

3.2 Aluminium films on polymer substrates

The results of section 3.1.2 reveal the laser machining process to impose an intrinsic limit on the laser irradiation power. This power is considerably less than is needed for laser-assisted metal ablation. The low-power property of this lithography method makes it especially suitable for structuring aluminium films on heat-sensitive materials such as polymers. Moreover, the process works in pure water without any addition of acids or lyes that may cause chemical damage to the substrate. In the following, successful fabrication of micrometer-sized aluminium electrodes on polymers such as PDMS and SU-8, a near-UV photore sist (LaBianca & Gelorme, 1995), is demonstrated.

3.2.1 Experimental

The patterning of the aluminium films was performed on a similar set-up as described in section 3.1.1. A 40x/0.75-NA Achromplan water immersion objective was used to focus the argon-ion laser beam of 488 nm wavelength to a spot of about 2.5 µm diameter onto the sample (Fig. 3.14). The specimen is fixed on a custom-made, piezoelectrically driven xy-scan stage composed of two closed-loop-controlled piezoelements (models P-841.40 and P-841.60, Physik Instrumente), providing a travel range of 90 µm x 60 µm. The motion of the stage is controlled by a LabView program.

The PDMS substrates (Sylgard 184, Dow Corning) were fabricated by curing a thin layer of the polymer on a clean cover slip. After solidification the flexible substrate was carefully detached from the glass and the flat surface formerly in contact with the cover slip used for metallization. The SU-8 substrate (IBM, Zurich) was fabricated by spin-coating the polymer (spin coater model KW-4A, Pi-Kem, Wem, England) on clean cover slips to a thickness ranging from 1-16 µm. The resist was prebaked at 95°C for 6 min, exposed to UV light and postbaked at 95°C for another 15 min.
Since polymers are known to show poor adhesion to metals, all substrates were treated by air plasma (Firebug, Nanotechnology Group, process parameters: air pressure: $4 \times 10^{-2}$ mbar, HF-voltage: 2 kV$_{pp}$, 10 kHz) prior to the aluminium coating. The plasma treatment improves the adhesion strength between the two materials (Gerenser, 1990), which minimises the probability of metal film detachment from the substrate during the laser processing. Since the thermal conductivity of our aluminium film ($\lambda_{Al} = 200$ W/mK, section 3.1.3) is considerably higher than of the polymeric substrates ($\lambda_{PDMS} = 0.18$ W/mK, $\lambda_{SU8} = 0.2$ W/mK), the temperature in the lateral vicinity of the process region increases far more in the metal film than in the glass or polymer substrate. This temperature difference causes uneven material expansion and interfacial stress, which then may lead to delamination of the metal if adhesion is not firm enough. The efficiency of the plasma treatment for PDMS and SU-8 was experimentally verified as shown in Fig. 3.15. The exposure of the polymers to air plasma increases the surface free energy. This assertion was verified by assessing the surface hydrophilicity via measurement of the contact angle of a drop of water deposited on the polymer surface (Israelachvili, 1991). The contact angle decreases for increasing hydrophilicity. A dramatic reduction of the contact angle was observed after 10 s of plasma exposure (Fig. 3.15a), providing evidence of enhanced surface free energy on PDMS and SU-8. After metallization of the polymers the adhesion strength between the metal film and the substrates has been investigated by determining the laser power limit of the aluminium corrosion process. The increased free
surface energy improves adhesion, which in turn reduces the thermal contact resistance between the aluminium and the polymer (Sakami et al., 2001). The reduced thermal contact resistance leads to a higher heat flux $\dot{Q}_s$ away from the heated metal film to the polymeric substrate (Fig. 3.4a). In order to achieve boiling of the water over the metal film, this heat loss must be compensated by increasing the incident laser intensity $I_0$. The laser power limit, which provokes boiling, is therefore an indicator for the adhesion strength between the metal and polymer. The higher the laser power limit observed, the better the adhesion. As shown in Fig. 3.15b, the laser power limit considerably increases for a plasma exposure time longer than 20 s, providing evidence of enhanced adhesion between the aluminium and PDMS or SU-8, respectively. This conclusion is further supported by the simultaneous increase of free surface energy (Fig. 3.15a) and laser power.
limit (Fig. 3.15b), which identifies the change in interfacial properties to be the reason for the reduced thermal contact resistance.

### 3.2.2 Results and discussion

Figure 3.16a shows a reflection light microscope image of an interdigitated electrode array on PDMS. This electrode configuration may find application in chemical sensing devices such as chemiresistors (Wohltjen et al., 1985). The polymer substrate was evaporation-coated by 60 nm of aluminium after curing. Some rippling of the soft polymer surface during vacuum treatment was observed. In spite of this surface roughness several electrode fingers and a rectangular clearing were successfully fabricated in one step by laser-assisted corrosion of the metal film in water. The dark areas in Fig. 3.16a correspond to the regions freed from aluminium. The width of the corroded gaps between the fingers measures about 1.5 μm. The utilised laser light of 488 nm wavelength is mainly absorbed by the aluminium film, while the PDMS substrate and water remain optically transparent. The laser processing power was set to 2.7 mW, which corresponds to the intrinsic power limit of the laser machining process. The writing speed amounted to 1 μm/s. Figure 3.16b shows a transmitted light microscope image of an interdigitated aluminium electrode on a 5-μm-thick SU-8 resist spin-coated on a glass substrate. A strip of 65-nm-thick aluminium of 100 μm width was first evaporation-coated onto the resist by shadow masking. The rectangular clearing and the gaps between the electrode fingers (bright areas in Fig. 3.16b) were subsequently corroded into the aluminium film. The metal film was processed at a laser power of about 17 mW and a writing speed of 3.5 μm/s. The irradiation power again corresponded to the intrinsic power limit of the process. It was higher than for PDMS due to stronger interfacial adhesion between the metal and the polymer (Fig. 3.15b).

On both substrates damage to the polymer surface was not observed. In contrast to conventional laser ablation the laser-assisted corrosion process generated no debris, which needed to be removed by lift-off of a protective resist layer that is applied on the metal film prior to the laser machining (Pethig et al., 1998). The reactants of the corrosion process are dissolved in the water and washed away from the surface.
Fig. 3.16a,b: Electrode patterning on polymers. a Reflected light microscope image of an interdigitated electrode array on PDMS. The dark areas correspond to regions freed from aluminium. b Transmitted light microscope image of an electrode array on SU-8 corroded into a 100-\(\mu\)m-wide strip of aluminium.

In contrast to PDMS the SU-8 near-ultraviolet photoresist (peak absorption: 365 nm) shows pronounced light absorption at the laser wavelength of 488 nm, which can lead to overheating of the resist substrate after the aluminium film is removed by corrosion and to thermal damage of the polymer. The polymer is convection-cooled at the water-substrate interface, however, below the surface the material may be undesirably heated above its degradation temperature of about 380°C. Such overheating can be avoided by scanning the laser spot at maximum possible velocity for a given laser power that still allows for corroding through the complete aluminium film in one step. In this case the exposure of the polymer to the laser irradiation is minimised. Notably, overheating of the substrate can be completely eliminated by changing the wavelength of the processing laser to green light (e.g. 532 nm). At this wavelength, the SU-8 substrate shows less absorption and the water preserves its transparency, both confining the laser-induced heating to the absorptive metal film. On the other hand, the light absorbing property of the polymer substrate provides advantages for three-dimensional microfabrication of electrode structures as demonstrated below. Thick-film resists such as SU-8 offer the inherent possibility of three-dimensional device design.

Figure 3.17a shows a transmitted light microscope image of a multilayered electrode structure. An interdigitated electrode array was fabricated by laser-assisted corrosion on a 16-\(\mu\)m-thick insulating SU-8 film spin-coated over a lower electrode fabricated via shadow mask evaporation on a glass substrate. The interdigitated electrode array extends in longitudinal
Fig. 3.17a,b: Double-layered electrode structuring on SU-8. a Transmitted light microscope image of 50-nm-thick interdigitated electrodes partly overlapping an electrode underneath a 16-μm-thick insulating SU-8 film (process parameters: laser power, 12.5 mW; writing speed, 2.0 μm/s). b Schematic of the multilayered electrode structure depicted in a.

direction over an edge of the lower electrode as shown in the schematic of Fig. 3.17b. This lower electrode covers the left side of Fig. 3.17a where only weak light transmission between the electrode array is observed. The right part shows intense light transmission due to the absence of any opaque electrode film.

The laser machining of multilayered electrode structures can suffer from the influence of back-reflected light from a lower electrode. The array shown in Fig. 3.17a exhibits uniform gaps between the individual fingers indicating constant process conditions during laser machining. The influence of back-reflected light from the underlying electrode on the manufacturing of the overlying array was therefore negligible. The diverging back-reflected laser light was of low intensity when it impinged on the overlying electrode due to the short focal depth of the laser spot with respect to the thickness of the intermediate polymer layer (Fig. 3.18a). However, for thinner intermediate SU-8 layers the back-reflected light can become intensely focused enough to considerably increase the temperature in
Fig. 3.18a-c: Influence of back-reflected light from a lower electrode on the laser processing of the overlying electrode for a thick intermediate SU-8 films and b thin polymer layers. c Laser power limit on the aluminium film on places with (white squares) and without (black squares) underlying electrode.

The process region on the overlying electrode (Fig. 3.18b). The additional heating enhances the aluminium corrosion process, which results in broader lines in the overlying electrodes in areas of multilayered electrodes compared to domains where a lower metal film is missing. This modulation of line width by back-reflected light from underlying electrodes is mainly an issue for intermediate polymer layers thinner than 7 \( \mu \text{m} \) as illustrated in Fig. 3.18c. The diagram depicts the laser power limit of the corrosion process determined on a 50-nm-thick aluminium film at places with and without an underlying electrode separated by a layer of SU-8 of variable thickness. In absence of an underlying electrode this laser power limit is not affected by the thickness of the polymer layer and measures about 16 mW in the average. If an underlying electrode is present, the laser
power limit is lower. It measures about 7 mW for intermediate polymer layers as thin as 2 \( \mu \text{m} \) and increases towards 16 mW for films thicker than 7 \( \mu \text{m} \), the same limit, which is observed for samples lacking another electrode layer. For thin polymer layers, the additional heating of the laser-irradiated metal film due to back-reflected light requires less incident laser power to heat the aluminium surface up to 100 °C than is needed for a single electrode layer. For polymer layers of thickness larger than 7 \( \mu \text{m} \) the difference of the laser power limit on single and double layered electrodes becomes insignificant, rendering the influence of the back-reflected light negligible. Note, that this threshold thickness can be reduced by using focusing objectives of high NA, which produce laser spots of shorter focal depth.

Electrodes on different layers can be connected via holes created by laser ablation in air of the intermediate polymer by taking advantage of the light absorption of the SU-8 resist at 488 nm wavelength and subsequent metallization. In this case absorption heating evaporates the material. The connecting holes were fabricated on the same set-up as was used for aluminium film patterning, except that the beam was concentrated on the polymer surface by a dry 40\( _{\times}^\circ \)/0.65-NA objective. Figure 3.19 shows a smooth-edged hole fabricated through a 1.4-\( \mu \text{m} \)-thick SU-8 layer at a laser power of 21 mW after metallization with 100 nm of aluminium. The SU-8 layer was applied on a glass substrate coated with 100 nm of aluminium. The electrical contact between the metal film on the glass surface and on the polymer layer through the connecting hole was verified by measuring

**Fig. 3.19:** Scanning electron microscope image of a connecting hole through a 1.4-\( \mu \text{m} \)-thick SU-8 film produced at a laser power of 21 mW. The taper angle of the hole edge measures about 11°.
Fig. 3.20a-d: Fabrication of a four-phase travelling wave electrode structure. 

a Schematic of the interdigitated electrodes energised by a double-layered bus-bar system. b Reflected light microscope image of the pump array in the image centre and the four bus-bars. c Close-up view of the pump array's bottom layer on glass, consisting of bus-bars no. 1, no. 2 and the interdigitated electrodes. The electrodes were structured by laser-assisted corrosion (laser power, 25 mW; writing speed, 1.8 μm/s). d Close up view of the electrode structure after spin-coating of a 1-μm-thick insulating SU-8 film over the bottom electrodes, drilling of connecting holes for electrodes no. 3 and no. 4 by laser ablation (laser power, 10 mW) and deposition of the bus-bars no. 3 and no. 4 by shadow mask evaporation.

the resistance. Increased laser power generally produced larger hole diameters. By slightly defocusing the laser beam after producing the initial hole the taper angle of the edges was further reduced, which enhanced the uniformity of the aluminium coating and electrical contact through the hole.

A possible application for connecting holes is shown in Fig. 3.20, which demonstrates the manufacturing of a four-phase electrohydrodynamic pump (Bart et al., 1990) based on an interdigitated electrode array energised by a double-layered bus-bar system. First, the electrode fingers outlined in Fig. 3.20a were patterned by laser-assisted corrosion on a 50-nm-thick and 220-μm-wide strip of aluminium film evaporated on a
glass substrate using shadow masking. The aluminium strip also acts as feed for the electrodes no. 1 and 2 (Fig. 3.20c). A 1-μm-thick insulating film of SU-8 resist was subsequently spin-coated over the electrodes and connecting holes for the electrodes no. 3 and 4 (Fig. 3.20d) were drilled by laser ablation. Finally 80-nm-thick bus-bars that energise the electrodes no. 3 and 4 via the connecting holes were deposited on the polymer by shadow masking (Fig. 3.20d). The time required to fabricate the electrode array, including the programming of the LabView-controlled laser machining set-up, the metal deposition and the laser processing, was about 6 h.

3.3 Rapid prototyping

The previous example for electrode fabrication shown in Fig. 3.20 demonstrates the feasibility of rapidly developing devices with multilayered and interconnected electrodes by combining the simple processes such as shadow mask evaporation, laser-assisted corrosion of aluminium and laser ablation of SU-8. In the following, the high flexibility of the laser-assisted corrosion process was applied to rapidly and inexpensively prototype a novel, asymmetric interdigitated electrode array for an electrohydrodynamic pump (Cahill, 2002).

The idea for the asymmetric electrode layout shown schematically in Figure 3.21a was basically adapted from Brownian ratchets (Astumian, 1997). Pairs of aluminium electrodes separated by a gap of several micrometers were repeated at intervals at least ten times larger than the small gap of the pair. Square waves of 90° phase difference were applied to each pair of electrodes, generating a travelling wave mainly localised to the small gap in the electrode pair. Due to the locally asymmetric field intensity between neighbouring electrodes a global net fluid flow in one defined direction was driven by electro-osmosis. The direction of pumping could be reversed by changing the phase of the square waves from 90° to -90°. An additional unstructured electrode acted as electrical ground. This set-up was much simpler than the previously fabricated four-phase electrohydrodynamic pump, since it allowed for simpler wiring and requires less manufacturing effort. Fig. 3.21b,c shows two asymmetric electrode arrays with different pair intervals corroded into a 50-nm-thick aluminium strip of about 230 μm width (laser power, 18 mW; writing speed, 1.8 μm/s) deposited by shadow mask evaporation on a glass substrate. The aluminium strip also acted as feed for the electrodes. The time required to program the LabView-controlled laser machining set-up and corrode the structure was
about 4 h. The device fabrication on such a short time-scale allows for rapid manufacturing of various electrode arrays of different pair intervals to optimise the device performance by testing and evaluation.

In Fig. 3.22 the pump performance of the array depicted in Fig. 3.21b was investigated. In this array the pairs of aluminium electrodes were separated by a 1.2-\(\mu\)m-gap and were repeated at about 24-\(\mu\)m-intervals, leaving a gap of 15 \(\mu\)m between individual pairs (Fig. 3.22a). The electrode array was covered by a glass slide coated with a 100-nm-thick, transparent ITO-layer acting as the electrical ground. Spacers between the cover glass and the substrate created a 70-\(\mu\)m-high channel for the fluid. Preliminary tests revealed the electrode structures fabricated by the simple laser-assisted corrosion process to operate properly. To this end, the channel was filled with water. The electrohydrodynamic flow was observed by tracking the motion of fluorescent colloidal particles of 100 nm diameter (Fluoresbrite, Polysciences Inc.) with an optical microscope (Nikon Eclipse 800) as they moved with the pumped fluid. The graph in Fig. 3.22b shows the particle motion along the pump array for a voltage signal of 3 V\(_{pp}\) and 350 kHz at
Fig. 3.22a,b: Performance testing of pump array. a Close-up view of the electrode array depicted in Fig. 3.21b. b Particle motion over the electrode array shown in a with the pump operating at +90° and -90° phase difference between electrodes no. 1 and no. 2 (square wave signal: 3 V$_{pp}$, 350 kHz).

+90° phase applied to the electrodes. The fluid was periodically accelerated over the electrode pair where the electrical field exhibited highest intensity. By changing the phase to -90° the fluid flow was reversed as predicted (Fig. 3.22b).
4 Subwavelength-sized aperture fabrication in aluminium by the use of an evanescent field

4.1 Introduction

In the previous chapter diffraction-limited patterning of planar aluminium films with features sizing in the range of 270 nm to several micrometers has been demonstrated. Here, the laser-thermal oxidation process was applied to remove the aluminium film from the tip of a pointed probe on dimensions below the diffraction limit of light. Vital to these experiments was the use of a confined heat source that affected only the aluminium at the tip apex.

Inexpensive and reproducible manufacturing of subwavelength-sized apertures in aluminium is a current issue in, e.g., the fabrication of probes for scanning nearfield optical microscopy (SNOM) or scanning thermal microscopy (Luo et al., 1996). In fact, broad application of SNOM would benefit from low-cost production of probes of high reproducible quality since the shape and size of the probe aperture exert crucial influence on the performance of the microscope. The nearfield aperture is commonly created by a simple shadowing scheme (Betzig et al., 1991), which, however, provides low reproducibility in aperture manufacturing. Another simple technique is based on scraping the aluminium away from the tip apex by moving the probe over a metal surface at high speed. Fig. 4.1 shows two SNOM probes made of an aluminium coated silicon nitride AFM cantilever with an aperture fabricated by rubbing the tip over a steel surface. Although a yield in aperture fabrication of almost 100% is achieved, the aperture formation is subject to stochastic processes in the removal of individual aluminium grains from the tip and thus exhibits low reproducibility. Therefore, favourable alternative techniques such as wet (Matsumoto & Ohtsu, 1996; Mononobe et al., 1997) or solid (Mulin et al., 1997; Bouhelier et al., 2001) electrolytic demetallization have been developed. These processes yield higher reproducibility and aperture definition but require either an elaborate set-up or consist of a time-consuming multistep lithography process including the use of resist and etchants. Recently, dry etching procedures based on focused-ion-beam (FIB) milling (Veerman et al., 1998; Zhou et al., 1999) and selective reactive ion etching (RIE) based on tip effects (Schürmann et al., 1999) evolved. These processes provide
Fig. 4.1a,b: Scanning electron microscope images of aperture probes fabricated by rubbing the aluminium away from the tip apex. The tips were scanned on a 10 \( \mu \text{m} \times 10 \mu \text{m} \) area of steel of 100 nm rms surface roughness with a scan velocity of 40 \( \mu \text{m/s} \) and applied load of 20 nN. The images show a side view of the aluminium-coated probe tip based on a silicon nitride cantilever. The resulting height of the silicon nitride tip freed from the aluminium cladding (arrow) is subject to large variations. It can range between 20-70 nm.

high aperture definition, however, they require expensive vacuum equipment.

In the following, a simple and inexpensive alternative to the above-mentioned techniques is presented that yields apertures of high quality and high reproducibility. The aperture is introduced into an aluminium film in one step by the low-power, laser-thermal oxidation process in water. The manufacturing set-up operates in common laboratory atmosphere and circumvents the use of resist layers and aggressive chemicals.

The crucial step in this aperture fabrication process consists of direct exposure of the aluminium-coated probe tip to an optical evanescent field that is created at a glass-water interface by total internal reflection of a blue laser beam (\( \lambda = 488 \text{ nm} \)) in the glass substrate (Fig. 4.2). To this end, the probe is immersed into pure water of pH = 7 at room temperature, where the aluminium forms a thin passivating oxide layer. By heating the metal at the probe tip close to 100 °C due to absorption of the evanescent light, the passivation is then inhibited and local corrosion of the metal occurs. Highly selective aluminium removal from the tip is achieved by the exponentially decaying nature of the evanescent field and the low light absorption property of water and glass. Because the irradiance decreases exponentially with increasing distance from the glass-water interface, the evanescent field acts as a heat source of limited spatial extent. Both glass (absorption coefficient at 488 nm: 0.002 cm\(^{-1} \), datasheet for BK7 from Schott,
Mainz, Germany) and water (0.0003 cm⁻¹, from Hale & Querry, 1973) exhibit high transparency for blue light, which confines heat production to the aluminium immersed in the thin optical nearfield.

The following sections provide a detailed description of the aperture manufacturing. Defined and reproducible aperture fabrication is demonstrated by the control of parameters governing the corrosion process such as the intensity and penetration depth of the evanescent field. Finally, the suitability of the aperture probes for SNOM imaging in transmission mode is verified.

4.2 Experimental

The SNOM probe used to demonstrate the aperture fabrication process is based on a commercial gold-coated silicon nitride cantilever used for contact atomic force microscopy. Note that the technique can also be applied to other types of probes such as fibres and micropipettes (Shalom et al., 1992). The AFM probe (NanoScope model NP-S, Digital Instruments Inc.) consists of a hollow pyramid with a typical base area of 4 μm x 4 μm and a full opening angle of 70° attached to a 200-μm-long, V-shaped cantilever. For use in a hybrid SNOM/AFM (Radmacher et al., 1994) the reflective gold layer was removed in aqua regia (3:1 HCl 37%, HNO₃ 65%) and the pyramidal tip was evaporation-coated with 120 nm of aluminium. During
metal deposition the V-shaped beam was shadow-masked by a razor blade to prevent the cantilever from bending due to interfacial stress (Fig. 4.3). The nearfield aperture was finally introduced at the tip apex by means of thermally induced corrosion.

The set-up for aperture fabrication is illustrated in Fig. 4.4. The evanescent field was produced by coupling a $p$-polarised laser beam (cw argon-ion laser, model 543-AP-A01, Melles Griot Laser Group, $\lambda = 488$ nm) with variable incidence $\theta_i$ via a lens and a prism into a microscope slide where it was internally reflected several times. The lens was adjusted to focus the

---

**Fig. 4.4:** Set-up for aperture fabrication (not to scale).
beam onto the upper slide surface where the first internal reflection on the upper side occurs. The diameter of the beam waist measured about 10 μm. Above the focal spot a 20 μl drop of ultrahigh-quality water was deposited. The aluminium-coated probe was fixed on a micrometer stage, immersed in the water and manually brought into contact with the slide surface in the centre of the reflected laser beam, thus exposing the tip apex to the highest intensity of the evanescent field. The loading force acting on the probe was set high enough to ensure contact between the tip and the glass substrate during the complete corrosion process. In order to facilitate the adjustment of the relative position of the laser beam and the SNOM probe, the set-up was mounted on an inverted light microscope (Zeiss Axiovert 100 TV, objective: 20x/0.40-NA Korr 0-1.5).

4.3 Results and discussions

Figure 4.5a shows a tip of an aluminium-coated AFM probe prior to the aperture fabrication. Upon exposure of the tip to the evanescent field, an aperture was formed within 5 s for a laser power of more than 80 mW and an angle of incidence larger than 61.5°. After the underlying silicon nitride tip apex was uncovered and touched the glass surface, the metal corrosion advanced away from the apex until the intensity of the evanescent field fell below a threshold required to produce enough heat in the aluminium film for metal removal. The oxidation process was thus self-terminating, providing highly selective demetallization at the tip. The height of the protruding tip can be defined by varying the intensity profile of the evanescent field. The intensity $I$ of the evanescent field perpendicular to the interface is described as follows (Hecht, 1998):

$$ I = I_0 e^{-z/d} \quad (4-1) $$

where $I_0$ denotes the intensity of the electromagnetic field at the glass-water interface, the variable $z$ denotes the vertical distance from the interface and $d$ the penetration depth of the evanescent field into the water. $I_0$ depends linearly on the power of the incident laser beam $I_L$ and in a more complex manner on the angle of incidence $\theta$: 
Fig. 4.5a-h: Aperture SNOM probe tips fabricated by selective corrosion in the evanescent field. The scanning electron microscope image in a shows an unprocessed probe. b-d, f and g show a lateral view and e a top view of processed probes. Aperture machining parameters were as follows: b laser power, 80 mW, angle of incidence of the totally reflected laser beam, 62°, exposure time: 10 s; c 90 mW, 62°, 10 s; d and e 90 mW, 62°, 15 s; f 90 mW, 61.5°, 10 s; g 90 mW, 63°, 10 s. The small grains visible on top of the aluminium grains of the tip in e originate from a thin layer of platinum, sputtered onto the probe to enhance imaging contrast in the electron microscope. h Summary of protrusion heights and corresponding fabrication parameters.
\[
\frac{I_0}{I_L} = \frac{(2n_g \cos \theta_i)^2}{\left[ n_w \cos \theta_i + n_g \sqrt{1 - \left( \frac{n_g \sin \theta_i}{n_w} \right)^2} \right]^2}
\]  
(4-2)

where \( n_w \) and \( n_g \) are the refractive indices of water and glass, respectively. Equation (4-2) is derived from the Fresnel’s law of \( p \)-polarised light refraction and reflection at an interface of two optical media (Hecht, 1998). \( I_0 \) reaches a maximum when \( \theta_i \) is equal to the critical angle and decreases to zero for \( \theta_i = 90^\circ \) as depicted in Fig. 4.6a for the glass-water interface. The graph shows the field enhancement \( I_0/I_L \) [Eq. (4-2)] of the incident laser light at the interface. The penetration depth of the evanescent field into the water can be described according to:

\[
d = \frac{\lambda}{4\pi} \left[ \frac{\sin^2 \theta_i}{\left( \frac{n_w}{n_g} \right)^2} - 1 \right]^{-\frac{1}{2}}
\]  
(4-3)

where \( \lambda \) is the wavelength of the laser beam in vacuum. Figure 4.6b shows the penetration depth versus the angle of incidence for a laser of 488 nm wavelength at a glass-water interface. The extension of the evanescent field is highest close to the critical angle and shortest at an incidence angle of \( \theta_i = 90^\circ \).

The intensity profile of the evanescent field can therefore be set by the power of the totally reflected laser beam and the angle of incidence \( \theta_i \). By increasing the beam power and decreasing the angle of incidence, the evanescent field becomes wider and more intense, which shifts the threshold intensity required to provoke heat-induced corrosion away from the interface and leads to a higher silicon nitride tip freed from the aluminium.

Figure 4.5b shows an aperture probe exposed for 10 s to an evanescent field created by a laser beam of about 80 mW power and an angle of incidence of 62°, which is close to the critical angle of a glass-water interface of 61°. The aluminium was removed only from the front-most part of the metallised tip up to the silicon nitride tip without uncovering it. The threshold intensity required for corrosion was therefore reached right at the glass-water interface. By increasing the laser power to about 90 mW, the intensity \( I_0 \) of the evanescent field at the interface was increased and the
threshold intensity was shifted away from the glass surface. This resulted in fully uncovered silicon nitride tips as shown in Fig. 4.5c-e. The exposure time was 10 s for the probe depicted in Fig. 4.5c and 15 s for the probes in Fig. 4.5d and e. The height of the tip measured about 30 nm for each of the three probes, providing evidence for the reproducibility and self-terminating property of the fabrication process. The diameter of the aperture depends on the diameter of the silicon nitride tip, which is defined by the cantilever fabrication process. Owing to variation in the shape of the tips, tip radius can vary between 5 nm and 40 nm; no clear relationship between protrusion length and aperture size was observed. The aperture diameter measured 38 nm for the probe depicted in Fig. 4.5c, 85 nm for the tip in Fig. 4.5d and 45 nm for the tip in Fig. 4.5e (see arrow). A steeper...
angle of incidence of 61.5° produced an evanescent field of higher penetration depth according to Eq. (4-3), resulting in a further shift of the threshold intensity away from the interface and a higher tip of 72 nm as depicted in Fig. 4.5f. The aperture diameter for this probe measured about 115 nm. The exposure time was 10 s. By moving the laser angle in the opposite direction towards shallower incidence, the penetration depth of the evanescent field is reduced, resulting in protrusion of about 20 nm height as shown in Fig. 4.5g. The aperture diameter of this probe measures about 50 nm, the exposure time was 10 s.

For inclinations smaller than 61.5° the evanescent field penetrates several hundred nanometer into the water and affects a considerably larger part of the probe tip, resulting in an unstable aperture formation processes. The aperture is constantly growing with increased exposure time since enough heat is generated in the freed silicon nitride substrate by light absorption to advance the metal corrosion continuously away from the apex. This leads to the removal of the cladding from the probe tip on the micrometer scale.

The protrusion heights attained by the evanescent light lithography are summarised in Fig. 4.5h. The experimental results show good agreement with theoretical calculations illustrated in Fig. 4.7. The diagram shows the
distance $z_T$ from the interface at a given laser power where the radiation intensity falls below the threshold $I_T$. This distance should correspond to the height of the silicon nitride tip freed from aluminium. The threshold intensity $I_T$ equals the intensity $I_0$ needed to corrode the aluminium off the probe depicted in Fig. 4.5b. For a laser of 80 mW power and 10 μm beam waste reflected at 62° incidence $I_T = 2.3 \text{ mW/μm}^2$ (Fig. 4.6a). The distance $z_T$ can be derived from Eq. (4-1) in combination with Eq. (4-2) and (4-3):

$$z_T = -d(\theta_i) \ln \frac{I_T}{I_0(\theta_i, I_s)}$$  \hspace{1cm} (4-4)

The height of the fabricated tips depicted in Fig. 4.5h and the threshold distance calculated in Fig. 4.7 both decrease with increasing angle of incidence and decreasing laser power.

Tip-induced field enhancement effects (Furukawa & Kawata, 1998) seemed to play only a minor role during aperture formation. This assertion has been verified by comparing the amount of radiation energy consumed for removal of a typical aluminium cap of the size shown in Fig. 4.8b with the energy required for corroding lines into a planar aluminium films by a focused laser beam. For the planar metal film the corrosion parameters of a 64-nm-thick sample are selected. The minimum line width $w_f$ achieved measured about 430 nm at a laser power $P_{lf}$ of 9.5 mW and a writing speed $v_f$ of 3.4 μm/s (section 3.1.2). This aluminium film exhibits similar lateral heat transfer properties as the cladding on the SNOM probe, which measures 69 nm in thickness in the case of a unidirectional deposition of 120 nm aluminium on the pyramid flanks tilted 35° with respect to the evaporation source. The energy consumed per volume, also called the specific energy, for writing the line into the planar aluminium film (Fig. 4.8a) with the laser machining parameters given above can be calculated as:

$$E_f = \frac{AP_{lf}}{v_f h_f w_f} = 20 \text{ mJ/μm}^3,$$  \hspace{1cm} (4-5)

where $A = 0.2$, the absorptivity determined in section 3.1.3. In Eq. (4-5) the beam diameter is assumed to be smaller or equal to the line width. In this case the complete laser power is consumed by the corrosion process.

In the following, the specific energy needed to remove the aluminium from the tip of a SNOM probe without a protruding silicon nitride tip such as shown in Fig. 4.5b is calculated. For this probe the complete metal cap
is corroded away at the glass-water interface. The loading force acting on the probe constantly moves the tip towards the interface, compensating for the removed material until the hard silicon nitride tip touches the glass surface. The energy to remove a thin layer of thickness $\Delta z$ from the tip in the time $\Delta t$ is given by:

$$\Delta E_p = I_T A x^2 \Delta t$$  \hspace{1cm} (4-6)$$

where $x^2$ is the area of the pyramidal tip in contact with the interface during the time $\Delta t$ (Fig. 4.8b). The intensity of the evanescent field corresponds to the threshold intensity $I_T$. Assuming a constant rate of metal layer removal, $\Delta t$ is:

$$\Delta t = \Delta z \frac{t_0}{h_p}$$  \hspace{1cm} (4-7)$$

where $t_0$ is the time to remove the whole aluminium cap and $h_p$ the total height of the pyramidal cap. The variable $x$ can also be written as a function of $z$:

$$x = z \frac{b}{h_p}$$  \hspace{1cm} (4-8)$$
where \( b \) is the base length of the pyramidal cap. By combining Eq. (4-7) and (4-8) with (4-6) and summing up the energies for each layer, the energy to remove the complete metal cap is calculated by:

\[
E_p = \sum I_T A \frac{b^2 t_0}{h_p^3} z^2 \Delta z = I_T A \frac{b^2 t_0}{h_p^3} \int_0^h z^2 dz = \frac{1}{3} I_T A b^2 t_0. \tag{4-9}
\]

The specific energy is then determined by dividing \( E_p \) by the volume of the aluminium cap:

\[
E_p' = I_T A \frac{t_0}{h_p} = 19mJ / \mu m^3 \tag{4-10}
\]

In the calculations presented above heat losses due to convection are assumed to be similar for planar films and the SNOM probe and have thus been neglected. Since the specific energy consumed for the corrosion of planar aluminium films [Eq. (4-5)] reveals to be in the same order of magnitude as for the metal tip of the SNOM probe [Eq. (4-10)], field enhancement was negligible for the overall result of the aperture manufacturing process. Some enhancement effects may be present in the early stage of the process when the metallised tip exhibits a tip radius much smaller than the wavelength of the laser light (Raether, 1988). However, with the corrosion advancing towards the silicon nitride substrate, the tip curvature is increased and the field enhancement considerably reduced.

During SNOM operation the hard silicon nitride tip protects the remarkably flat metallic aperture rim (Fig. 4.5e) from degeneration by friction, thus improving the lifetime of the probe. Moreover, the protrusion ensures defined position of the rim in reference to the point of contact of the probe tip with the sample, which enhances the stability of SNOM and AFM image acquisition.

### 4.4 SNOM experiment

#### 4.4.1 Microscope set-up

The suitability of the aperture probes for SNOM imaging was tested on a custom-made hybrid SNOM/AFM microscope (Fig. 4.9). This instrument
Fig. 4.9: Set-up of hybrid SNOM/AFM microscope (not to scale).

has been built (Fleseriu & Binzel, 1998; Keller, 1999) and implemented (Haefliger, 2000) earlier at the Nanotechnology Group, ETH Zurich. It allowed for simultaneous topographical, nearfield and farfield optical measurements of transparent samples. The device consisted of a scan stage and a laser optics head incorporating the cantilever holder, an optical beam deflection system and the tip illumination optics, and was directly attached on top of an inverted optical microscope (Zeiss Axiovert 100 TV). The optical microscope facilitated specimen positioning and the alignment of the SNOM and AFM lasers with respect to the SNOM probe. The illumination optics, consisting of an optical fiber, a beam expander and a convex lens (NA = 0.15), focused a cw argon-ion laser beam of 488 nm wavelength into the hollow pyramidal tip of the SNOM probe. The light coupled out of the aperture at the tip apex was collected by the microscope objec-
Five (Zeiss, 40×/0.65-NA Achroplan or 100×/1.30-NA Plan-Neofluar) and projected onto a confocal photodetector (PINJ-5DP/SB, UTD Sensors Inc.). The confocal arrangement prevented scattered light from impinging onto the photodetector and imposing noise on the optical signal. The sample was placed on a piezoelectrically driven, highly integrated monolithic scan stage that was capable of moving the specimen in three dimensions over a range of 90 μm × 90 μm × 12 μm. The probe was scanned over a specimen in contact mode at constant force using an optical lever system well known from the AFM (Meyer & Amer, 1988). A laser beam emitted from a diode laser (670 nm wavelength, 3.5 mW) was coupled into the probe illumination path by a dichroic beam splitter and focused onto the cantilever beam near the pyramidal tip. The reflected light was collected by the focusing lens, passed to the beam splitter and reflected onto a quadrant photodiode. To selectively transmit only the laser beam used as the optical lever, the photodiode was covered with a narrow band pass filter (10 nm bandwidth at 670 nm, Chroma Technology Corp.). This greatly improved the signal to noise ratio for the topographical signal. Since both, optical beam deflection and tip illumination system used the same focusing optics, a compact and rigid microscope set-up resulted, which minimised measurement errors due to oscillations and thermal expansion of the set-up. The scan stage and data acquisition were controlled by commercial scanning probe electronics (RHK SPM1000).

4.4.2 Measurements

In order to assess the SNOM probe performance, an adequate test sample was required, which enables the determination of the true optical resolution. The so-called “latex sphere projection pattern” is a specimen, which has frequently been used for simultaneous assessment of optical and topographical resolution. The pattern consists of nearly triangular aluminium patches of several nanometers in thickness on a glass slide arranged in a hexagonal pattern. It was fabricated by unidirectional deposition of the metal over a monolayered hexagonal crystal of latex beads on the slide. After metal coating, the beads were removed by ultrasonication in water, leaving a metal pattern on the glass substrate. Figure 4.10 shows a simultaneously acquired topographical and nearfield optical image of such a projection pattern made of 8-nm-thick aluminium, evaporated over beads of 500 nm (Fig. 4.10a,b) and 220 nm (Fig. 4.10c,d) diameter. The aperture for the SNOM probes used for imaging these samples was fabricated by the
rubbing scheme as shown in Fig. 4.1. However, in these measurements the correlated topographical and optical contrast revealed to be a major issue in determining the optical resolution. Due to the exponential decay of the nearfield at the probe aperture, the optical signal reacts very sensitively, e.g., on variations in tip-sample separation that occur upon the motion of the tip over the edge of the aluminium pattern. As pointed out by Hecht et al. (1997), this so-called $z$-motion artifact can generate features in the optical image that are highly correlated with the structures in the topographic image. The presence of this artifact is not obvious because the sample topography is part of its optical structure. Thus an image showing only fea-

**Fig. 4.10:** a,b Simultaneously acquired $1.5 \mu m \times 1.5 \mu m$ a topographical and b nearfield optical image of a latex bead projection pattern made of spheres of 500 nm diameter ($z$-scale in a 10 nm, in b arbitrary unit). The light has been collected by a Zeiss 40x/0.65-NA objective. c,d Simultaneously acquired $0.5 \mu m \times 0.5 \mu m$ c topographical and d nearfield optical image of a projection pattern made of beads of 220 nm diameter ($z$-scale in a 10 nm, in b arbitrary unit). The light was collected by a Zeiss 100x/1.30-NA objective. The rings in c,d originate from residues of the latex beads.
Fig. 4.11: Optical microscope image of a SNOM probe tip (cantilever edge marked by white lines) illuminated by laser light and in contact with a microscope cover slip. The light is transmitted through the aperture (arrow) but also penetrates through the cladding at the pyramidal tip (marked square) and part passes beside the cantilever, causing stray light.

Features that correlate to topographical characteristics can be a genuine nearfield optical picture, a pure $z$-motion artifact image, or a superposition of both. If the optical image exhibits the same resolution than the topographical picture the optical signal is likely to be affected by crosstalk. The images in Fig. 4.10a,b show a topographical edge resolution of 24 nm and an optical edge resolution of 30 nm. The edge resolution is determined by measuring the horizontal distance between 10 % and 90 % of the total step height or intensity change over the metal edge, respectively. The topographical and optical resolutions in the images of Fig. 4.10b,c are 12 nm and 16 nm, respectively. The optical resolution achieved in Fig. 4.10 was rather astonishing since the aperture diameter of the probes fabricated here was usually larger than 30 nm (Fig. 4.1 and Fig. 4.5). Furthermore, the small difference between topographical and optical resolution and the high optical contrast may provide further evidence of image crosstalk. In fact, images of a latex bead projection patterns with a similar high optical contrast have also been observed by Danzebrink et al. (1998). The authors attributed this untypically high image quality to topographical artifacts, which arose from stray-light of the illuminating laser around the probe tip. In the vicinity of the nearfield aperture the intensity of this stray-light was modulated by interference effects appearing between probe and sample, and was superimposed on the weak genuine nearfield signal. Since the illumination laser used here produced considerable stray-light (Fig. 4.11), the optical images measured in Fig. 4.10 may therefore also originate from interference phenomena. In conclusion, the origin of the astonishingly
clear and noise-free optical images in Fig. 4.10b,d can not be clearly identified. They may be attributed to genuine nearfield optics, interference phenomena or the superposition of both.

To circumvent any topographical crosstalk Hecht et al. (1997) suggested to perform nearfield optical microscopy in constant height mode, i.e., without z-motion of the probe. The probe is scanned at a constant set point several tens of nanometers above the sample surface. However, constant height mode imaging was impossible with the silicon nitride cantilevers used here due to insufficient beam stiffness. Capillary condensation between the probe tip and the sample surface forced the soft probe into contact with the specimen surface. Thus, in order to give a precise, quantitative assessment on the resolution capability of the SNOM probes the fabrication of a test sample with uncorrelated topographical and optical contrast was devised.

A better measure of the optical resolution can be achieved by imaging a point-like light source such as individual fluorescently labelled biomolecules (Veerman et al., 1998). Owing to the small dimensions of the molecules, z-motion artifacts are negligible. Moreover the fluorescent read-out eliminates any influence of stray light. However, the sensitivity of the photodetector used in the microscope set-up here was insufficient to detect the light emitted by a single labelled molecule. Also the imaging of fluorescent nanospheres of 20 nm diameter (Höppener et al., 2002) embedded in a 100-nm-thick film of PMMA deposited on a glass slide has failed due to insufficient detector sensitivity.

Successful quantification of the probe resolution has finally been achieved in transmission mode on a novel high-contrast, “topography-free” test specimen adapted from Kalkbrenner et al. (2000) (Fig. 4.12). The specimen was produced by first sputter-coating 5 nm of gold onto a freshly cleaved mica sheet. A drop of NaCl solution was deposited onto the gold surface and dried by pressurised air, leaving salt crystals of several 100 nm in diameter behind (Hartmann et al., 1993). The crystals acted as a mask for the subsequent evaporation-deposition of 8 nm of aluminium. After the sample was rinsed in water dissolving the salt crystals, a perforated aluminium film was left. This specimen was finally glued metal face down onto a glass cover slip using a transparent resin (Epo-tek 301-2, Poly-science, Switzerland) and the mica was mechanically stripped off by adhesive tape. The uncovered template-stripped gold surface is almost as flat as the mica itself but exhibits sharp optical contrast (Fig. 4.12b).
Fig. 4.12: a High-contrast, "topography-free" test sample fabrication: (1) sputter-deposition of 5 nm gold on mica, (2) deposition of salt crystals, (3) evaporation-deposition of 8 nm aluminium, (4) lift-off of salt crystals in water, (5) gluing of glass slide on metal film by transparent resin, (6) mechanical stripping of mica from metal film. b Farfield transmitted light image (objective: Zeiss, 40×/0.65-NA) of the test specimen shown in step (6) of a. Bright areas correspond to holes in the 8-nm-thick, perforated aluminium film.

Figure 4.13a shows a combined image of simultaneously measured topographical and nearfield optical data of the test specimen acquired by a SNOM probe with an aperture fabricated by aluminium corrosion. The transmitted light has been collected by a Zeiss 100×/1.30-NA objective. The topography exhibits only small height variations that do not correlate with the optical contrast produced by the perforated aluminium film. This uncorrelated contrast provides evidence for an authentic nearfield optical
Fig. 4.13: a Combined SNOM/AFM image of simultaneously acquired transmitted nearfield optical signal and topographical data on a 1.0 µm x 1.0 µm area of the test sample depicted in Fig. 4.12b (z-scale is 10 nm). b Profile plot of the optical nearfield signal along the white line drawn in a. An edge resolution of 85 ± 6 nm is determined by measuring the horizontal distance between 10 % and 90% of the total intensity change over the edge of a hole in the aluminium film.

The edge resolution is determined to 85 ± 6 nm (Fig. 4.13b), which compares well with previously reported resolution capabilities of aperture SNOM probes fabricated by more elaborate processes (Veerman et al., 1998; Genolet et al., 2001).

The optical efficiency of the probe used for the experiment amounted to about 10^{-7}. This transmission coefficient was measured in the farfield by the microscope objective and thus only includes light of propagating nature
coupled out of the aperture. At the first glance the low optical efficiency seemed to be rather surprising since probes made of tapered fibres provide throughputs of up to $10^{-5}$ (Veerman et al., 1998). The taper angle of the cantilevered probe used here was larger than for pulled fiber probes of a typical full angle ranging between $5^\circ$ and $20^\circ$, moving the cut-off of the propagating waves in the probes here closer to the aperture. A higher power transmission would therefore be expected (Novotny et al. 1995). However, the hollow pyramidal tip acts as a concave lens, refracting the light away from the tip apex such that only a small amount of the incident laser power is reaching the aperture. The efficiency of the probes used here can be improved, e.g., by placing a micrometer-sized bead into the hollow tip by a micro-robotic pipette (Haefliger et al., 2003a). The bead acts as a ball lens, focusing the incident light onto the probe tip. Nevertheless, the results presented in Fig. 4.13 demonstrate the apertures fabricated by corrosion in the evanescent field to be suitable for reliable SNOM imaging with competitive resolution power.
5 Nanolithography of planar aluminium films

5.1 Introduction

The patterning of planar aluminium films with features sizing below 100 nm requires a heat source of nanometer extent in at least two dimensions. In the case of evanescent light lithography described in chapter 4, a subwavelength-sized heat source was achieved in only one dimension. Three-dimensional nanolithography was nevertheless made possible by the pointed shape of the substrate, which allowed for selective heating of only the front-most part of the tip in the evanescent field.

For nano-structuring of planar films two thermochemical lithography schemes (Fig. 5.1) were taken into account here. The schemes rely on physical nearfield interaction of a scanning probe tip and the aluminium film to be structured. The nearfield thermoconducting lithography method illustrated in Fig. 5.1a is based on heat conduction through a nanometer-sized physical contact area between the probe and the metal film in water. The heat is produced in the probe tip by absorption of laser light, transported to the tip apex by diffusion and then transferred into the aluminium film, inducing local corrosion underneath the probe tip. Scanning probe tips have already been used for thermomechanical surface modifications such as STM-assisted melting of metallic glasses in vacuum (Staufer et al., 1988) and nanoindentation of PMMA films by an AFM tip in air (Mamin & Rugar, 1992). In the latter experiment the tip of the AFM probe was

![Fig. 5.1a,b: Thermochemical nanolithography schemes. a Nearfield thermoconducting lithography. b Nearfield optical lithography.](image-url)
Fig 5.2a,b: Problems in nearfield thermoconducting lithography. a The hot probe induces convective heat flux from the tip to the aluminium film, decreasing, b, the corrosion selectivity in the metal film.

Heated by a focused laser beam that was absorbed by the probe material. In a next step the authors improved the lithography process by developing probes which can be heated by built-in resistors (Chui et al., 1996). Preliminary experiments on AFM-assisted corrosion of aluminium films were performed with silicon probes used for contact AFM (Ultra-levers ULCT-AUHW, Park Scientific Instruments) heated by green laser radiation (Verdi-V10, Coherent Inc. Laser Group, $\lambda = 532 \text{ nm}$). The surface machining in water prevented the use of resistively heated cantilevers as described in Chui et al. (1996) due to short-circuiting of the heaters by the surrounding medium. An additional, water-tight sealing of the cantilever structure would be required. However, the results revealed the selectivity of this lithography scheme to be insufficient for reliable nano-scale corrosion of the metal surface. Heat-induced water convection around the hot probe tip caused a considerable heat transport from the probe via the water to the aluminium surface on an area of up to several tens of micrometers (Fig. 5.2). This additional heat flux prevented a confined metal heating of the surface underneath the probe tip to create nano-scale holes. Experiments on 15-nm-thick aluminium films rather produced micrometer-sized depressions with poor edge definition. To prevent convective heat flux further experiments were performed in air of about 90 % humidity. In this case, the water and oxygen needed for the oxidation reaction (Fig. 2.1) is supplied by capillary condensation at the probe tip in contact with the metal film. The process has potential application in writing metal oxide lines into the aluminium film, since the reactants of the corrosion process
are not washed away by the water. However, as preliminary experiments revealed, the water meniscus at the hot probe tip seemed to be too small to provide enough reactants for the metal oxidation. At room temperature the radius of the water meniscus, the so-called Kelvin radius (Israelachvili, 1991), measures about 12 nm. At 100 °C this radius is theoretically reduced to 9 nm. The silicon probes were treated in air plasma to enhance the wettability of the tip, but the experiments produced no surface modifications on 5-nm-thick aluminium films.

Therefore, further attention was focused on the nearfield optical nano-lithography scheme shown in Fig. 5.1b. In this method the heat is directly produced at the location where it is needed for surface machining, namely in a subwavelength-sized volume of the aluminium film. The confined heat source is created underneath an AFM tip by an intense optical nearfield. This localised nearfield is produced by tip-induced enhancement of an evanescent field originating from a laser beam, which is totally internally reflected at the glass-aluminium-water interface (Furukawa & Kawata, 1998). The selectivity of this lithography scheme mainly depends on the degree of field enhancement and is hardly affected by convective heat flux through the medium above the aluminium film. This set-up has already been successfully used to modify the surface of polymers by metal-coated AFM probes in air (Iwata et al., 2002, Tarun et al., 2002). The following sections provide further details on the AFM-assisted laser machining process and the successful nanostructuring of aluminium films below the wavelength of light.

5.2 Experimental

Thin aluminium films of 20 nm thickness were deposited by vacuum evaporation (BAE 120, Balzers) on microscope cover slips that were cleaned in oxygen plasma prior to the coating. The patterning of the samples was performed on a set-up, which basically combined the total internal reflection set-up used for SNOM probe manufacturing (Fig. 4.4) with the scan stage and laser optics head of the hybrid SNOM/AFM microscope (Fig. 4.9).

The sample was placed on a beam-coupling unit made of a microscope slide and a prism (Fig. 5.3) with the gap between the slide and specimen filled with immersion oil (518 N, Zeiss). The beam-coupling unit was then fixed on the scan stage built for the custom made hybrid SNOM/AFM (section 4.4.1). An evanescent field was produced on the sample surface by
Fig. 5.3: Set-up for AFM-assisted nanolithography of aluminium films (not to scale).

guiding a \( p \)-polarised laser beam of 532 nm wavelength (Nd:YVO\(_4\) laser, Verdi-V10, Coherent Inc. Laser Group) with variable incidence angle \( \theta_i \) via a lens and a prism into a microscope slide where it was internally reflected several times. The lens was adjusted to focus the beam onto the aluminium surface on the sample. The diameter of the beam waist measured about 18 \( \mu \)m. Above the focal spot a drop of ultrahigh-quality water was deposited. A contact-AFM probe was fixed on the laser optics head of the hybrid SNOM/AFM (section 4.4.1), immersed into the water and brought into contact with the slide surface in the centre of the reflected laser beam, exposing the tip to the highest intensity of the evanescent field. The alignment of the laser beam and the AFM probe was facilitated by the inverted light microscope (Zeiss Axiovert 100 TV, objective: 20x/0.40-NA Korr 0-1.5). For aluminium corrosion the probe was kept in contact with the sample at constant force by the optical lever feedback (Meyer & Amer, 1988). The closed loop operation enabled the probe to follow the surface topography and to compensate for the material removal underneath the tip.
5.3 Theoretical considerations

5.3.1 Probe

The probe material and shape of the tip apex exerts considerable influence on the field enhancement magnitude. In the following, some criteria are elaborated to provide a basis for selecting the appropriate tip material and if applicable, the tip coating for reliable AFM lithography. The optical field distribution and enhancement at a probe tip with radius much smaller than the wavelength of light was calculated in great detail by computational analysis of the Maxwell differential electromagnetic equations for probes made of silver (Denk & Pohl, 1991), gold (Novotny et al., 1997), platinum-iridium and dielectric materials (Furukawa & Kawata, 1998). However, to gain insight into the mechanisms governing the field enhancement at the probe tip here, a simple system, for which an analytical solution exists, can be considered (Fig. 5.4). Equation (5-1) describes the local enhancement factor of the field intensity at the tip of a single sphere or prolate spheroid illuminated by light polarised parallel to the longest axis (Raether, 1988):

\[
\frac{(E_{tip})}{(E_0)} = \frac{\varepsilon_1/\varepsilon_0}{1 + (\varepsilon_1/\varepsilon_0 - 1)M + i(\varepsilon_1^*/\varepsilon_0)M + D \varepsilon_1^*/\varepsilon_0 + iD(1-\varepsilon_1/\varepsilon_0)}
\]

(5-1)

Fig. 5.4: Prolate spheroid illuminated from the side (wave vector k). The electromagnetic field \(E_0\) is enhanced at the spheroids tips \(E_{tip}\).
The dimension of the object is much smaller than the wavelength of the illuminating light. $E_{\text{tip}}$ denotes the electromagnetic field at the particle tip and $E_0$ the field of the incoming light. The dielectric constants of the surrounding medium and the spheroid are described by $\varepsilon_0$ and by the complex $\varepsilon_i$, respectively:

$$\varepsilon_i = \varepsilon_i' + i\varepsilon_i''.$$

The factor $M$ denotes the demagnetising factor, which is tabulated for general ellipsoids in Osborn (1945) for different aspect ratios $a/b$ of the spheroid axes $a$ and $b$ (Fig. 5.4). $D$ is the radiation damping factor which depends on the object volume $V$ and the wavelength $\lambda$ of the illuminating light:

$$D = \frac{4\pi^2 V}{3 \lambda^3}.$$

In the case of metal particles the incoming electromagnetic field can induce coherent fluctuations of electron charges on the metal boundary, which are called surface plasmon oscillations. For a negative real part of the object’s dielectric constant $\varepsilon_i$, these fluctuations can be excited at resonance. If the damping factor of the metal, expressed by the imaginary part of the dielectric constant, $\varepsilon_i''$, is small compared to $\varepsilon_i'$, the surface plasmon oscillations considerably contribute to the field enhancement at the tip as shown in Fig. 5.5a for gold. For a prolate spheroid with an aspect ratio of $a/b = 2$ and $b = 20$ nm a maximum enhancement of about 700 is achieved in water. The enhancement factor was calculated according to Eq. (5-1), with the dielectric constants extracted from Weaver et al. (1981). However, regarding practical applications of gold for an AFM probe coating, the metal exhibits poor mechanical properties such as low stiffness and poor adhesion. Silver, which is also an excellent material for surface plasmon enhancement due to low damping, shows insufficient immunity in air and water since it tends to form a thin passivation layer. Figure 5.5b shows the field enhancement in water of a spheroid with $a/b = 2$ and $b = 20$ nm made of platinum. This metal is chemically inert and provides good adhesion properties. However, the damping factor of platinum is much larger than for gold, allowing for a less pronounced field enhancement with a maximum of about 12. In the case of dielectrics such as silicon nitride (Fig. 5.5b, $a/b = 2$, $b = 20$ nm, in water) the enhancement factor depends
Fig. 5.5: Field enhancement factor for a gold and b platinum and silicon nitride in the VIS-NIR spectrum. The calculation was performed for a spheroidal particle of \( a/b = 2 \) in water according to Eq. (5-1).

only on the tip shape due to the limited mobility of the electrons which prevents plasmon resonance. The field enhancement was calculated to a constant value of about 3 in the complete VIS-NIR spectrum and is thus smaller than for metals.

Figure 5.6 depicts the field enhancement factor for spheroids of different aspect ratios \( a/b \) in water at light of 532 nm wavelength calculated according to Eq. (5-1) for platinum and materials commonly used for AFM probes. The appropriate dielectric constants are listed in Tab. 5.1. For \( a/b = 1 \) the radius of the sphere was set to \( b = 20 \) nm. The axis \( b \) of spheroids with higher aspect ratio was reduced to give the same object volume. The constant volume eliminates the influence of radiation damping \( D \) on the results plotted in Fig. 5.6. With increasing aspect ratio \( a/b \) the enhancement improves for metallic as well as for dielectric spheroids. The
Fig. 5.6: Enhancement factors in water at \( \lambda = 532 \text{ nm} \) for spheroids of different aspect ratio and material calculated according to Eq. (5-1) with dielectric constants given in Tab. 5.1.

strongest enhancement is achieved for silicon, followed by platinum and silicon nitride. However, silicon is a very reactive material forming a thin oxide layer on the surface when exposed to air during storage. This passivation can transform the tip apex into silicon dioxide. As shown in Fig. 5.6., this material provides very poor enhancement due to a small ratio \( \varepsilon_1/\varepsilon_0 \). Surface oxidised silicon AFM probes are thus unsuitable for field enhanced optical nanomachining. The best candidates are composed of sharp tips with a small opening angle made of bare silicon or coated with an inert, mechanically stable metal such as platinum.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \varepsilon_1' )</th>
<th>( \varepsilon_1'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon*</td>
<td>17.2</td>
<td>0.24</td>
</tr>
<tr>
<td>Silicon dioxide (SiO(_2))*</td>
<td>2.13</td>
<td>0</td>
</tr>
<tr>
<td>Silicon nitride (Si(_3)N(_4))*</td>
<td>3.6</td>
<td>0</td>
</tr>
<tr>
<td>Platinum***</td>
<td>-8.73</td>
<td>14.85</td>
</tr>
</tbody>
</table>

Tab. 5.1: Dielectric constants of materials used for AFM probes and coating. * from Herzinger et al. (1998), ** from Palik (1998), *** from Weaver et al. (1981).
5.3.2 Incidence angle

As already demonstrated in the evanescent light lithography procedure for SNOM probes described in section 4.3, the incidence angle $\theta$ of the laser exerts crucial influence on the evanescent field created at the interface of totally internally reflection (Fig. 4.6). However, in contrast to the SNOM probe lithography scheme, the evanescent field in the AFM-assisted lithography method here was produced at an interface composed of glass, aluminium and water. The introduction of a metal layer between two dielectric media increased the complexity in the behaviour of the evanescent field due to surface plasmon excitation in the aluminium film. In the following, the internal light reflection at the glass-aluminium-water interface was experimentally and theoretically investigated and the optimum laser incidence angle was determined, which provides the maximum selectivity for field-enhanced optical nanolithography.

The glass-aluminium-water system described here was analysed in analogy to an attenuated total reflection (ATR) configuration of the ‘Raether-Kretschmann’ type (Raether, 1988). ATR couplers are generally applied for exciting surface plasmons in thin metal films. To this end, the metal film is deposited on one side of a glass prism. Inside the prism a laser beam is totally internally reflected at the metal-coated surface and generates the surface plasmons. The intensity of the light reflected from the surface depends on the amount of electromagnetic energy coupled to the electrons of the metal film. Strong coupling can be observed when the evanescent light wave along the surface matches the plasmon frequency. The wave vector of this light is described as (Fig. 5.7):

$$ k_x = \sqrt{\varepsilon_0 \frac{2\pi}{\lambda} \sin \theta_l} $$  \hspace{1cm} (5-4)

where $\varepsilon_0$ is the dielectric constant of the glass substrate ($\varepsilon_0 = 2.30$). The plasmon excitation and corresponding reflection intensity thus depend on the angle of incidence of the laser beam. The relative intensity $R$ of the reflected light can be calculated by the following set of equations, derived from Fresnel’s law for reflection of $p$-polarised light at a two-boundary interface (Raether, 1988):

$$ k_{zi} = \sqrt{\varepsilon_i \left( \frac{2\pi}{\lambda} \right)^2 - k_x^2}, \hspace{0.5cm} i = 0,1,2 $$  \hspace{1cm} (5-5)
Fig. 5.7: Attenuated total reflection of light at a metal surface.

\[ r_{ik} = \left( \frac{k_{zi} - k_{zk}}{\varepsilon_i - \varepsilon_k} \right) \left( \frac{k_{zi} + k_{zk}}{\varepsilon_i - \varepsilon_k} \right), \quad i,k = 0,1; 1,2 \]  \hspace{1cm} (5-6)

\[ R = |r_{012}|^2 = \frac{r_{01} + r_{12} \exp(2ik_{zi}h)}{1 + r_{01}r_{12} \exp(2ik_{zi}h)}, \]  \hspace{1cm} (5-7)

where \( \varepsilon_i \) is the complex dielectric constant of the metal layer according to Eq. (5-2) and \( \varepsilon_2 \) the dielectric constant of the water (\( \varepsilon_2 = 1.79 \)). \( k_{zi} \) is the projection of the wave vector perpendicular to the interface in each medium as illustrated in Fig. 5.7 and \( r_{ik} \) the Fresnel’s reflection coefficient at the glass-metal (\( r_{0i} \)) and metal-water (\( r_{12} \)) boundary layer, respectively. The variable \( h \) denotes the thickness of the metal film. In Fig. 5.8a the intensity of the reflected light (\( \lambda = 532 \) nm) for a glass-aluminium-water system with a metal layer of different thickness is calculated. The computational analysis was experimentally verified on a simple, custom-built ATR device, using the same laser as for the nanolithography set-up shown in Fig. 5.3. Best correlation between experiment and calculation was achieved for a dielectric constant of \( \varepsilon_i = -35 + i11 \) for aluminium, which is close to the published value of \( \varepsilon = -39 + i10 \) (Weaver et al., 1981). Deviations are due to radiation losses originating from imperfect metal adhesion on the glass substrate and roughness of the metal surface.
Fig. 5.8: a Measured (dots) and calculated reflectivity [lines, Eq. (5-7)] of a glass-aluminium-water interface for aluminium of different thickness. Best correlation between calculation and measurement was achieved for a dielectric constant of $\varepsilon_1 = -35 + i/11$ for aluminium. b Field enhancement due to surface plasmons, calculated for the glass-aluminium-water system [Eq. (5-9)]. c Estimated selectivity of the tip-enhanced lithography process by means of the ratio between field enhancement and absorption [Eq. (5-10)].
For thin metal films around 20 nm thickness the reflection shows a pronounced minimum at an incidence angle between 65° and 68°. The energy conservation requires:

\[ R + A + T = 1, \quad (5-8) \]

where \( A \) is the relative absorption and \( T \) the transmission. Since in the total reflection condition \( T = 0 \), the light that is not reflected, is completely absorbed in the metal film. The electromagnetic energy is transferred to the plasma and dissipated into heat. The surface plasmons lead to an enhanced electromagnetic field on the metal surface, which reaches its highest intensity when the reflected light diminishes. The relative field enhancement \( |t_{012}|^2 \) for \( p \)-polarised light is calculated by (Raether, 1988):

\[ |t_{012}|^2 = \frac{(1 + r_{01})(1 + r_{12}) \exp(ik_{z1}h)^2}{1 + r_{01}r_{12} \exp(2ik_{z1}h)}, \quad (5-9) \]

plotted in Fig. 5.8b for the same system as in Fig. 5.8a. For aluminium films thicker than 45 nm the absorption and enhancement phenomena are less pronounced due to increased radiation damping.

For AFM-assisted laser lithography an intense evanescent field is desirable to produce a strong locally enhanced nearfield at the probe tip. As Fig. 5.8a and 5.8b demonstrate, this can be achieved by illuminating the aluminium film close to the angle where the reflectivity reaches its minimum. However, at this incidence angle the electromagnetic energy absorbed by the aluminium film reaches its maximum, which can lead to heat-induced corrosion of the metal film in the laser-irradiated spot. The additional heating of the aluminium in the vicinity of the AFM tip reduces the selectivity of the nearfield-enhanced, thermochemical lithography process. A higher selectivity is achieved at incidence angles close to the critical angle as demonstrated in Fig. 5.8c. The process selectivity is determined by means of the ratio between the normalised field enhancement factor \( |t_{012}|^2_n = |t_{012}|^2 / |t_{012}|^2_{\text{max}} \) and the relative absorption:

\[ s = \frac{|t_{012}|^2_n}{1 - R}. \quad (5-10) \]
Fig. 5.9a,b: Intensity of light scattered by the AFM probe. The curve shows the intensity along a horizontal axis through the tip apex for a cantilever made of a silicon nitride and b silicon. The tip position was at 0 µm.

For aluminium films around 20 nm thickness an incidence angle of about 63° is advised. At this angle the reflectivity culminates (Fig. 5.8a), while some field enhancement is already present, leading to an optimum selectivity. Metal films thicker than 45 nm can be processed at an angle of 65°, which corresponds to the angle of maximum field enhancement. For these aluminium films a culmination of reflectivity close to the critical angle is not observed.

5.4 Results and discussion

Figure 5.9 shows the intensity of the light scattered by an AFM probe tip made of silicon nitride (NanoScope NP-S, Digital Instruments Inc., Fig. 5.9.a) and silicon (Ultrasharp NSC12, Mikromasch, Fig. 5.9b) placed in the centre of the laser beam reflected at the glass-aluminium-water interface. The intensity was measured by collecting the light by the 20x-objective (Fig. 5.3) and projecting it onto a CCD camera (LV 8500, Leutron Vision). The curves in Fig. 5.9 reflect the light intensity extracted from the camera image along a horizontal axis through the tip apex. The aluminium film measured about 20 nm and the angle of incidence was 63°. The scattered light intensity is proportional to the intensity of the localised nearfield at the probe tip. As Fig. 5.9 illustrates, the nearfield at a silicon nitride tip is about twice as intense as for a silicon tip. The tip-induced field enhancement at a silicon probe was thus less efficient, suggesting an oxidised tip
Fig. 5.10: Accumulation of material (arrow) at the tip of a platinum-coated silicon nitride cantilever after contact with the aluminium film in water.

apex. The experimental results show good qualitative agreement with theoretical calculations of the tip enhancement for spheroids made of Si$_3$N$_4$ and SiO$_2$ (Fig. 5.6). Due to the weak enhancement efficiency of oxidised silicon probes the performance of platinum-coated silicon nitride probes (NanoScope NP-S, Digital Instruments Inc.) was further investigated. However, metal-coated probes revealed to be unsuitable for nano-scale corrosion of aluminium films in water as demonstrated in Fig. 5.10. The aluminium film and the platinum coating on the probe formed a galvanic cell when immersed together into water. The standard electrode potential of platinum and aluminium in water of 25 °C is 1.188 V and -1.676 V, respectively (Bard & Faulkner, 2001). Upon contact of the probe tip with the aluminium film a corrosion current flowed through the contact area, which led to the rapid deposition of a considerable amount of presumably aluminium oxide on the tip apex (Fig. 5.10). The accumulated material hinders the tip apex from penetrating into the corroded holes in the aluminium film. This limits the etch depth, since the enhanced optical nearfield is highly localised at the apex and it reduces the structuring resolution due to additional light scattering at the deposition. The following experiments in nanolithography were thus conducted with probes made of bare silicon nitride.

Figure 5.11 demonstrates the influence of the incidence angle on the process selectivity as theoretically investigated in Fig. 5.8. The AFM image in Fig. 5.11a shows an 11-nm-deep hole of 30 nm diameter (full width at half minimum) corroded into a 20-nm-thick aluminium film by thermo-chemical apertureless nearfield optical microscopy. The metal film was exposed 4 s to a laser beam of about 28 mW power (wave vector $k$ in
Fig. 5.11: a AFM image of a 11-nm-deep hole of 30 nm diameter corroded into a 20-nm-thick aluminium film (z-scale, 13 nm). Process parameters: laser power, 30 mW; angle of incidence, 64°; exposure time, 4 s. b Transmitted light image of processed aluminium film in the vicinity of the hole depicted in a.

Fig. 5.11). This laser power was close to the power limit that caused boiling of the water above the aluminium film. The incidence angle was set to about 64°, which is off the optimum angle providing high selectivity (Fig. 5.8c). In fact, as illustrated by Fig. 5.11b the area surrounding the tip was considerably affected by laser-thermal oxidation induced by the totally reflected laser beam. The oxidised material is identified by the enhanced light transmission of the metal film in the vicinity of the tip. In particular, severe oxidation occurred in a horse-shoe-shaped area around the tip location. The origin of this enhanced oxidation is not fully understood but may arise from interference of surface plasmons on the aluminium film due to plasmon scattering at the tip apex.

At the optimum incidence angle of 63° for 20-nm-thick aluminium films (Fig. 5.8c) the metal film could be successfully structured without observing the oxidation phenomena depicted in Fig. 5.11b. The absorption in the metal film was reduced, enabling a higher process selectivity as predicted in section 5.3.2. The laser power limit measured about 75 mW. Figure 5.12 demonstrates the patterning of a 20-nm-thick aluminium film with holes of 40 nm diameter at a laser power of 40 mW. The hole depth depended on the laser exposure time as illustrated in Fig. 5.12a,b and d. The depression in the AFM image of Fig. 5.12a measures 12 nm and was fabricated by exposing the aluminium film 5 s to the laser irradiation. A longer exposure time resulted in a deeper hole as depicted in Fig. 5.12b. The irradiation time was 10 s, yielding a depression penetrating through the complete aluminium film of 20 nm thickness. The AFM images were acquired right after the corrosion experiments with the same probe as used for the
Fig. 5.12a-d: Corroding holes into a 20-nm-thick aluminium film by thermochemical apertureless nearfield optical microscopy. 

a AFM image of a 12-nm-deep hole of 40 nm diameter. Process parameters: laser power, 40 mW; incidence angle, 63°; exposure time, 5 s. 
b AFM image of a 20-nm-deep hole of 40 nm diameter. Exposure time, 10 s. (z-scale in a and b: 30 nm). 
c Lateral view by SEM of the AFM probe tip used to corrode the holes in a and b. The small grains covering the probe surface originate from a thin layer of platinum, sputtered onto the probe to enhance imaging contrast. The larger grains on the flanks of the probe correspond to aluminium oxide residues of the corrosion process. Refer to the co-ordinate system in a and c to determine the relative position of the probe and aluminium film during laser machining. Due to the localised nature of the tip-enhanced nearfield the structure corroded into the aluminium film resembles the shape of the tip apex (tail-like feature in b, see arrow). 
d Hole depth achieved at different exposure times.

surface modification and utilising the custom-built AFM integrated in the laser machining set-up depicted in Fig. 5.3. The hole depth shows almost a linear dependency on the exposure time as demonstrated in Fig. 5.12d. A similar behaviour was observed for nanomachining of polymer films with
apertureless nearfield optical microscopy in the total reflection configuration by Iwata et al. (2002).

The diameter of the fabricated holes mainly depended on the tip shape of the AFM probe as shown in Fig. 5.12b,c. The hole and adjacent shallow tail structure (arrow in Fig. 5.12b) resemble the curvature of the probe tip imaged from the side in Fig. 5.12c. Refer to the co-ordinate system for the relative position of the probe and the sample during laser machining. Owing to the localised nature of the tip-enhanced nearfield, only the material close to the tip apex is affected by heat-induced corrosion, leading to the observed footprint of the tip shape in the aluminium film. The flat apex corresponds to the original shape of the tip prior to the surface machining. The hardness of the silicon nitride substrate and low contact force between probe and sample rendered abrasion of the material during film processing negligible. The hole in Fig. 5.12b reveals the process to be capable of patterning 20-nm-thick metal films with structures of an aspect ratio of 1:2. This compares well with aspect ratios achieved by SPM-assisted anodic oxidation processes. In these lithography schemes metal films of 3-8 nm thickness are commonly patterned at an aspect ratio ranging between 1:5 (Snow et al., 1996) and 1:14 (Boisen et al., 1998).

Moving the AFM probe at a speed of 100-200 nm/s over an 18-nm-thick aluminium film enabled the writing of subwavelength-sized lines into the metal surface as demonstrated in Fig. 5.13. The experiments were performed at a laser power of about 60 mW and an incidence angle of 63°. At a writing speed of 136 nm/s a 5.5-nm-deep line (Fig. 5.13a) of about 20 nm width (Fig. 5.13d) was achieved. A slower scan velocity of 125 nm/s resulted in a deeper trough of 13 nm depth (Fig. 5.13b) and 42 nm width (Fig. 5.13e). At a writing speed below 115 nm/s lines of 18 nm depth (Fig. 5.13c) and 130 nm width (Fig. 5.13f) were attained. The slower the scan speed the higher the radiation energy absorbed per unit line length and the deeper the advance of the corrosion into the metal film. An overview on the line depth and corresponding scan velocity is given in Fig. 5.13g. The experiments in Fig. 5.13a,b and c were performed with different AFM probes of different tip shape. The tip radius can vary between 5 and 40 nm, contributing to a large variation in the line width.

To verify the nearfield optical origin of the lithography process the specific energy consumed for writing lines into a 18-nm-thick film was compared to farfield laser machining of a 15-nm-thick planar aluminium film. Both metal films exhibit comparable heat transfer properties. The minimum line width \( w_f \) achieved by farfield lithography measured 266 nm at a laser power of 1.7 mW and a writing speed \( v_f = 25.5 \mu m/s \) (section 3.1.2).
Fig. 5.13a-g: Corroding lines into an 18-nm-thick aluminium film by thermochemical apertureless nearfield optical microscopy. a AFM image of a 5.5-nm-deep line of 20 nm width. Process parameters: laser power, 60 mW; incidence angle, 63°; scan velocity, 136 nm/s (z-scale: 15 nm). b AFM image of a 13-nm-deep line of 42 nm width. Scan velocity, 125 nm/s (z-scale: 25 nm). c AFM image of a 18-nm-deep line of 130 nm width. Scan velocity, 115 nm/s (z-scale: 30 nm). d-f Profile plot along the white line drawn in a-c. The line width is determined as the full width of the trough at half-minimum. g Line depth attained at different scan velocities.
Since the line width was smaller than the diameter of the laser focus only part of the beam power was actually used for machining. This laser power was estimated to 0.81 mW, utilising the approximation of the beam profile outlined in section 3.1.3. The specific energy can then be calculated by Eq. (4-5), where $A = 0.2$ (section 3.1.3), $P_L = 0.81$ mW and the film thickness $h_f = 15$ nm:

$$E' = 1.6 \text{ mJ/} \mu \text{m}^3.$$  \hspace{1cm} (5-11)

The specific energy for the nearfield optical laser-machining is estimated for the 42-nm-wide line of 13 nm depth shown in Fig. 5.13b. It is produced by the localised nearfield below the AFM tip acting as the confined heat source. The diameter $2r$ of the probe tip is estimated to 40 nm, which corresponds to the width of the fabricated trough. The maximum intensity of the nearfield $I_{Tip}$ is calculated as

$$I_{Tip} = \eta_{Tip} \eta_{SP} I_0,$$  \hspace{1cm} (5-12)

where $I_0$ is the maximum intensity of the laser beam perpendicular to a cross-section of $\theta_i = 63^\circ$ incidence with reference to the beam axis:

$$I_0 = \frac{2P_L \cos \theta_i}{\pi w^2}.$$  \hspace{1cm} (5-13)

$P_L$ denotes the laser power and $w = 9$ $\mu$m the radius of the beam waist of the laser spot on the glass-aluminium-water interface (section 5.2). $\eta_{SP}$ corresponds to the field enhancement factor due to the surface plasmons on the aluminium film and $\eta_{Tip}$ the tip enhancement factor. For $\theta_i = 63^\circ$ and a film thickness of 18 nm, $\eta_{SP} \approx 4$ (Fig. 5.8b, $|t_{0/2}|^2$ for a 20-nm-thick aluminium film). In the case of a silicon nitride tip of 40 nm diameter $\eta_{Tip} \approx 3$ as shown in Fig. 5.6. Using Eq. (5-12), (5-13) and the above-mentioned enhancement factors the intensity of the nearfield becomes $I_{Tip} = 2.6$ mW/$\mu$m$^2$. This value is in the same range than the threshold intensity $I_T = 2.3$ mW/$\mu$m$^2$ calculated for the SNOM probe manufacturing process (section 4.3). Assuming that the area of the nearfield measures the same size than the tip diameter, the specific energy to corrode the line of Fig. 5.13b equals:
\[ E_i' = \frac{A I_{\text{tip}} r^2 \pi}{v_i w_i h_i} = 9.6 \text{mJ} / \mu \text{m}^3, \]  

(5-14)

where \( A = 0.2 \), the scan velocity \( v_i = 0.125 \text{ nm/s} \), the line width \( w_i = 42 \text{ nm} \) and the line depth \( h_i = 13 \text{ nm} \). Since the specific energy consumed for the farfield and nearfield optical structuring of planar aluminium films ranges in the same order of magnitude, the AFM-assisted lithography scheme is evidently based on thermo-chemically induced corrosion due to absorption of light from the localised nearfield below the probe tip. This assertion is further supported by the fact, that the intensity of the nearfield is in the same range than the threshold intensity needed to induce corrosion of the aluminium cladding on the SNOM probe tip. The influence of heat, which is produced in the tip of the silicon nitride probe by absorption of the evanescent light and transported to the aluminium film is therefore negligible. This has also been observed during the SNOM aperture fabrication procedure at laser incidence angles larger than 61.5°. Above this angle the process proved to be self-terminated. The heat generated in the small silicon nitride protrusion was insufficient to advance the corrosion away from the tip apex (section 4.3).

A major problem of AFM-assisted nearfield optical corrosion by the use of silicon nitride cantilevers arose from the electrostatic attraction of the probe material and the aluminium hydroxide in the processed region on the aluminium film. The aluminium hydroxide exhibits a positive surface charge in neutral water of \( \text{pH} = 7 \) due to an isoelectric point (IEP) of about \( \text{pH} = 9.2 \) (Robinson et al., 1964). During laser-machining the generated oxide tended to adhere to the probe tip as seen in Fig. 5.12c. The larger grains on the probe flanks are very likely to represent accumulations of aluminium oxide. This observation suggests the probe surface to be charged negatively. For silicon nitride probes an IEP between \( \text{pH} = 6 \) and 8.5 has been observed (Senden & Drummond, 1995), supporting this assertion. The aluminium oxide regularly stuck to the tip apex, which caused similar problems as observed for metallised probes (Fig. 5.10), namely reduced lateral etch resolution and limited corrosion depth. Moreover, the tip contamination by the oxide made imaging of the corroded structures with the same probe as used for processing rather difficult. Some improvement in tip contamination and imaging stability was achieved by processing the aluminium film in an aqueous solution of about \( \text{pH} = 10 \). This solution was produced by adding NaOH to pure water. At \( \text{pH} = 10 \) the aluminium hydroxide and silicon nitride surface were negatively charged,
Fig. 5.14a,b: Corrosion of a 20-nm-thick aluminium film by thermo-chemical apertureless nearfield optical microscopy in an aqueous solution of pH = 10. a AFM image of a 12-nm-deep hole of 67 nm width and 130 length. Process parameters: laser power, 40 mW; incidence angle, 63°; exposure time, 5 s. (z-scale: 30 nm). b Lateral view by SEM of the AFM probe tip used to corrode the hole in a. The small grains covering the probe surface originate from a thin layer of platinum, sputtered onto the probe to enhance imaging contrast. The larger grain close to the tip apex corresponds to an aluminium oxide residue of the corrosion process. Refer to the co-ordinate system in a and b to determine the relative position of the probe and aluminium film during laser machining.

resulting in a repulsion of the two materials. As Fig. 2.2 reveals, the aluminium film is attacked by corrosion at this pH value, however, the rate of dissolution observed was very slow (several nm per hour). The metal film could thus be patterned by the apertureless nearfield optical microscope at high selectivity as demonstrated in Fig. 5.14. The AFM image in Fig. 5.14a shows a 67-nm-wide and 130-nm-long hole of 12 nm depth corroded into a 20-nm-thick aluminium film. The metal film was irradiated for 5 s by a laser of 40 mW power at the angle of incidence of 63°. The heat generated by the optical nearfield locally accelerated the corrosion rate of the aluminium producing the subwavelength-sized hole. After the film processing the AFM probe revealed only weak contamination by aluminium oxide as illustrated in Fig. 5.14b. Similar to the experiments shown in Fig. 5.12 the hole in Fig. 5.14a reflects the shape of the AFM tip apex. Refer to the co-ordinate systems for the appropriate orientation of the probe and the aluminium film during processing.

Fig. 5.14 demonstrates the feasibility of aluminium film processing occurring completely in the corrosion domain by accelerating the reaction
rate. Further research on topics such as the buffering of the aqueous solution and the design of a receptacle that avoids evaporation of the liquid and a change in pH during processing would be required to optimise the process for reliable nanoscale lithography.
6 Laser-thermal corrosion of metals other than aluminium

The simple laser-assisted corrosion process presented here enables inexpensive, fast and flexible patterning of aluminium thin films. The extension of this process to other materials would increase the versatility of the process and meet further needs in low-cost machining of various metal films used in microelectromechanical systems.

6.1 Overview

The results of the corrosion experiments performed with various metals are summarised in Tab. 6.1. The materials were either sputtered or evaporated on glass substrates to a film of 50-100 nm thickness and laser-machined on the set-up illustrated in Fig. 3.14. The processed samples were inspected by transmission light microscopy. Because oxidised or corroded areas show less light absorption, successful laser machining was recognised by an increase in transmitted light intensity through processed domains. The results obtained in water were verified by laser machining of the metal film in air at the same irradiation power, that enabled surface modification in water. If oxidation also occurred in air, the surface machining observed in water was either completely of photochemical origin (Bäuerle, 2000), or a combination of photochemical and -thermal processes.

Tungsten revealed to be the only element among the investigated metals listed in Tab. 6.1, which allowed for pure laser-thermal processing. The metal corrodes in neutral water at room temperature by dissolution as $\text{WO}_4^{2-}$ (Pourbaix, 1974). This process occurs, however, at very low reaction rate. After immersion of a 50-nm-thick tungsten film into water for one hour an inspection by optical microscopy revealed no degeneration of the metal surface. Upon heating of the metallization close to 100 °C by laser light, the corrosion rate was considerably increased and the complete film was locally removed by dissolution with high selectivity. The same transmitted light intensity in processed areas was observed than in un-coated regions on the substrate. Tungsten films could not be oxidised in air, providing evidence that the observed process is purely laser-thermal in nature. Further experiments on laser-assisted corrosion of tungsten are presented in section 6.2.
Reactivity in neutral water at 25 °C
- Au, Pt: immune
- Ag: immune
- Cu: immune
- Ta, Ti, Cr: passivated
- W: corroded

Reactivity in neutral water at 100 °C
- Au, Pt: immune
- Ag: passivated
- Cu: immune
- Ta, Ti, Cr: passivated
- W: corroded

Laser-thermal oxidation
- Au, Pt: NO
- Ag: YES
- Cu: NO
- Ta, Ti, Cr: YES
- W: YES

Laser-chemical oxidation
- Au, Pt: NO
- Ag: NO
- Cu: YES
- Ta, Ti, Cr: NO
- W: NO

Tab. 6.1: Summarised results from laser-induced oxidation of various metal thin films.

The noble metals such as gold and platinum resisted laser-induced corrosion since they exhibit immunity in neutral water at room temperature and at 100 °C. Silver and copper are known to be immune at room temperature, but formed a passivating oxide layer of Ag₂O or Cu₂O, respectively, (Pourbaix, 1974) when heated close to 100 °C by laser light. Oxidation through a complete, 50-nm-thick silver film was unsuccessful. In fact, the silver oxide layer seemed to maintain a chemically stable thickness estimated to several nanometers. The laser machining caused only very weak enhancement of light transmitted through the processed regions. Copper in the contrary allowed for through-oxidation of a complete, 20-nm-thick metal film. However, in contrast to silver, copper films could also be oxidised in air. The surface modification was therefore dominated by photo-chemically induced oxidation. This photo-chemical contribution is particularly interesting since it revealed some pronounced differences to the photo-thermal process governing the aluminium corrosion and was thus worthwhile to be further investigated. Some results are provided in section 6.3.

Tantalum, titanium and chromium form a very stable passivating oxide layer of Ta₂O₅-H₂O, TiO₂-H₂O or Cr(OH)₃, respectively, when immersed in neutral water at room temperature (Pourbaix, 1974). Upon heating of the metal films close to 100 °C by laser irradiation the passivation was enhanced until the oxide layer reached again a thermodynamically stable thickness. Similar to the silver films, the optical transmission in the processed regions was only weakly enhanced. The stable oxide thickness was therefore estimated to only several nanometers, preventing oxidation.
through complete metal films of several tens of nanometers. Laser-induced oxidation of tantalum, titanium and chromium in air was not observed.

6.2 Laser-thermal corrosion of tungsten thin films

Fig. 6.1 shows the tungsten-water phase diagram at room temperature revealing the metal to corrode in neutral water. This corrosion rate is very slow but can be accelerated by heating the system to 100 °C. Laser light focused on the tungsten film is converted into heat, which considerably enhances the chemical reaction rate and allows for highly selective metal dissolution as demonstrated in Fig. 6.2. Fig. 6.2a shows an AFM image and Fig. 6.2b a transmitted light microscope image of two lines written into a 20-nm-thick tungsten film at a speed of 1.24 μm/s and a laser power of 2.1 mW. This laser power corresponded to the power limit of the process. For laser machining the set-up illustrated in Fig. 3.14 was used.

Fig. 6.1: Phase diagram for the tungsten-water system at room temperature. The diagram is adopted from Pourbaix (1974). The metal corrodes in neutral water at 25 °C (pH = 7, black square) by dissolution as WO$_4^{2-}$. 
6.3 Laser-machining of copper thin films

Copper thin films have recently attracted considerable interest in the semiconductor industry due to improved performance and reliability of copper wires compared to aluminium electrodes (Geppert, 1998). Moreover, copper is one of the most studied metals for laser-assisted oxidation. Cuprous oxide ($\text{Cu}_2\text{O}$) finds applications, e.g., in optical and semiconductor devices due to a band gap of 2.17 eV (Palik, 1998), which corresponds to 571.7 nm wavelength. This band gap in the orange-yellow domain of the VIS light regime is the key to the laser-chemical processing of the copper films observed here. Theoretical calculations (Brook, 1972) predict the metal to remain chemically immune against oxidation in neutral water at room temperature and at 100 °C as illustrated in the copper-water phase diagram in Fig. 6.3. Absorptive heating of the copper film is thus expected to exert only minor influence on the oxidation of the metal film. This assumption is supported by the fact, that copper could also be oxidised in air (Tab. 6.1). The oxidation phenomenon observed here is rather explained by photo-electronic effects (Wautelet, 1990). Since the blue laser light of 488 nm ($= 2.54$ eV) nearly matches the band gap of cuprous oxide, photons can enhance the oxidation rate of the metal film by electron excitation. The copper interacts directly with the dissolved oxygen in water without needing the water molecules for the chemical reaction.
Figure 6.3: Phase diagram for the copper-water system at room temperature (solid lines) and 100 °C (dashed lines). The diagram is adopted from Brook (1972). The metal is immune in neutral water at 25 °C (pH = 7, black square) and at 100 °C (pH = 6.12, white square).

Figure 6.4 shows a transmitted light microscope image of two 400-nm-wide cuprous lines written at a speed of 0.6 μm/s into a 15-nm-thick copper film in neutral water. The lithography was carried out on the same set-up as shown in Fig. 3.1. The laser power was set to 2.2 mW, which corresponded to the maximum possible power that avoided boiling of the water above the metal film. Figure 6.5 summarises the minimum line width and corresponding writing speed that allowed for oxidising through the complete metal film of thickness ranging between 5 nm and 20 nm in one step. In contrast to aluminium films (Fig. 3.5) the line width was independent of the thickness of the metal film, although the thermal conductivity of copper ranges in the same order of magnitude (λ = 401 W/mK) than the one of the aluminium (λ = 200 W/mK, section 3.1.3). The process was thus unaffected by heat diffusion in the metal film, providing evidence of a photochemical origin of the surface laser-machining.
The laser-chemical process was further investigated by changing the wavelength of the tuneable argon-ion laser to the 457 nm (= 2.71 eV) and 514 nm (= 2.41 eV) line (Fig. 6.6). At each wavelength the laser was operated at the highest possible power that avoided water boiling. This guaranteed for the same irradiation power absorbed in the copper film in all experiments. By tuning the laser to 514 nm the maximum writing speed to through-oxidise a 15-nm-thick copper film increased from 0.6 μm/s at 488 nm to 1.1 μm/s. The accelerated scan speed indicates an enhancement

![Fig. 6.4: Transmitted light microscope image of laser-chemically oxidised lines into a 15-nm-thick copper film. Image size is 10 μm x 10 μm.](image)

![Fig. 6.5: Minimal achievable line width (solid curve) and corresponding scan velocity (dashed curve) for copper films of different thickness processed close to the laser power limit. The line width was measured by light microscopy (Zeiss, 100×/1.30-NA oil).](image)
of the oxidation rate due to an improved electron excitation. The energy of the photons of 514 nm wavelength is closer to the band gap energy, thus enhancing the production of charge carriers in the cuprous oxide and improving the efficiency of the photo-chemical oxidation process. By tuning the laser wavelength away from the band gap energy, the oxidation efficiency is reduced, resulting in a maximum scan velocity of 0.41 μm/s. These findings provided further evidence for a photo-chemical oxidation mechanism governing the copper oxidation. Moreover, the results presented in this section revealed distinctive differences in the laser-induced oxidation process of copper and aluminium films, which support the theoretical considerations performed in chapter 2 on the laser-thermal origin of the aluminium oxidation mechanism.
7 Conclusion

A simple, inexpensive, one-step lithography process for aluminium thin films based on laser-thermal corrosion in water was presented.

This patterning method was used to create nano- and micrometer-sized aluminium electrodes on glass substrates. The process imposed an intrinsic power limit on the incident laser irradiation, which measured only several milliwatts. If the metal surface was heated up to 100 °C, the water evaporated and interrupted the corrosive reaction. The saturation of the laser power limit observed for aluminium films thicker than 70 nm was successfully verified by a computational heat transfer analysis.

The low-power property of the corrosion process enabled the structuring of aluminium films directly on sensitive polymer substrates. Soft polymers such as PDMS covered with a structured metallization may also offer usage as lithographic masks in conformal contact to the surface, allowing inexpensive replication of structures into uneven resist layers by UV lithography. By taking advantage of the absorptive property of dyed polymers such as SU-8 and the intrinsic 3D processing capability of laser machining, connecting holes between electrode layers were fabricated, allowing for interconnected multilayered electrode design. The simplicity and flexibility of the laser-assisted corrosion process allowed for rapid and inexpensive prototyping of electrode structures for the development of microsystems. Successful prototyping and preliminary testing of an asymmetric electrode array for electrohydrodynamic pumping was demonstrated.

The laser machining technique was applied for low-cost fabrication of apertures for SNOM/AFM probes based on silicon nitride cantilevers coated with aluminium. An evanescent optical field at a glass-water interface was used as heat source to corrode the aluminium away from the tip apex of the probe. The diameter of the aperture was given by the lateral dimension of the protruding silicon nitride tip. The height of the silicon nitride protrusion was defined by the intensity profile of the evanescent field, which was controlled via the power and angle of incidence of a totally reflected laser beam. Due to the self-terminating property of the corrosion process, high selectivity in metal removal and high reproducibility in tip height was achieved. Based on successful experiments on planar polymer substrates, applicability of this method to probes made of SU-8 (Genolet et al., 2001; Kim et al., 2001) is expected. Parallel processing of a
complete wafer of SNOM probes may be realised by using flexible substrates with integrated microlens arrays (Wu et al., 2002).

Planar aluminium films were patterned with features of dimensions beyond the diffraction limit of light by an optical nearfield created at the tip of an AFM probe. Although the intensity of optical nearfields is known to be very weak, the high power density enabled local heating of the aluminium surface to about 100 °C. The nearfield at the probe tip was generated by tip-induced enhancement of an evanescent wave, which was created on the aluminium surface by totally internally reflection of a laser beam at the water-aluminium-substrate interface. In order to provide high process selectivity, a calculation of the reflectivity and field enhancement at the aluminium film was performed, revealing the optimum incidence angle of the internally reflected laser beam to range close to the critical angle. 20-nm-thick aluminium films were patterned with lines of 20-130 nm diameter. Aluminium films structured with subwavelength-sized perforations can be used for contact masks in parallel nearfield optical lithography (Alkaisi et al., 1999) or directly as etch mask for RIE processes (Boisen et al., 1998), and for single point contacts. The set-up realised for laser machining allows for either farfield processing directly by the totally internally reflected laser beam without the AFM probe, or nearfield optical lithography with the probe introduced in the evanescent field. The combination of these two processes leads to an efficient metal patterning method, which takes advantage of the speed of direct laser writing and the nanometer resolution of the AFM lithography.

The laser-thermal oxidation process was used to corrode tungsten and to oxidise the surface of silver, chromium, tantalum and titanium, demonstrating the versatility of the lithography technique.

Further applications of the heat-induced corrosion process may include the use of aluminium thin films as sacrificial layer, especially for polymeric devices. Moreover, parallelisation of the lithography scheme utilising a polymeric stamp (Xia & Whitesides, 1998) and a hot plate may be devised. Upon conformal contact of the elastomer stamp with the aluminium film, the recessed regions on the stamp surface and the metal film form a microfluidic network which can be filled with water. The stamp and aluminium film are then placed on a hot plate where the aluminium wetted by the water in the capillaries is attacked by corrosion. To remove the reaction products the microfluidic network can be connected via a three-dimensional channel network in the stamp (Jo et al., 2000) to an external water pump that generates a continuous fluid flow.
References


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