

Michael Köhler

Etching in Microsystem Technology

Translated by Antje Wiegand

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Preface

Microcomponents and microdevices in the form of electronic chips are very common nowadays in everyday life. They are of decisive importance in computers, but also in other devices. They are found in science and technology, in trade and industry, at official departments, at schools and in vocational training, that means in all parts of public, economic and private life.

For some time, however, microcomponents have been used not only for electronic devices. Miniaturized data processors, sensors and actuators of all kinds, even complete microsystems are developed and gain more and more applications. The specific functions of all of these minute devices depend strongly on the selection and combination of the materials they are built of, i.e., the chemical and physical solid-state properties of these materials and their styling. Normally this styling is performed by lithographic etching processes. Hence these etching processes take up a key position in microfabrication.

The microtechnical etching of functional patterns is a typical interdisciplinary area. The actual dissolution of the material is connected as a rule with a change of matter and is therefore of chemical nature. The chemical action during etching in liquid media can be described by the methods of coordination chemistry, electrochemistry, and surface chemistry. In dry-etching procedures plasma physical, plasma chemical, and photochemical processes prevail. The change of matter in either kind of etching processes is accompanied by some physical processes that concern, e.g., fluid and gas dynamics, as well as solid state physics. The purpose of etching is a microtechnical pattern. Special devices are used for the microlithographic process and its control, the functional principles of these are dealt with by engineering. Chemistry, physics and engineering science supply jointly the basis for microtechnical etching processes.

This book is an introduction to the essential microlithographic etching methods. Its purpose is the presentation of the characteristics and the area of use of the respective etching processes. The basic scientific principles of significant processes are dealt with, and their importance for the respective microtechnical etching process and its product, i.e. the pattern or structure in the microdevice, is explained. The joint discussion of physical-chemical and microtechnical aspects should strengthen the understanding of the methods, their advantages and possible applications and their specific characteristics.

The book is divided in two sections. The wet and dry etching processes are presented in a general section. A kind of catalogue of etching bath compositions, etching instructions and parameters is given in a second, more special section. This list should enhance the comprehension of the general section and also give an overview of essential data for the practical microtechnical training as well as for microtechnical research and development. The book is intended for engineers, technicians and natural scientists, who work in the area of microtechniques and deal with microtechnical etching methods. The book also is addressed to students, preferentially those of physics, engineering or chemistry, as their fields will be shaped more and more by the application of microsystems in years to come, and therefore specific microtechnical solutions and new developments in microsystems technology will be in demand.

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Ag	GaP	Pb,Zr _x Ti _{1-x} O ₃ (PZT)
Al	GaSb	PSG (Phosphosilicate Glass)
Al(Ti)	Ge	Pt
(Al,Ga)As	Ge _x Si _{1-x}	
Al _{0.5} Ga _{0.5} P		
(Al,Ga,In)P	Hf	RuO ₂
(Al,In)As	HgTe	
AlInN		Sb
Al _{0.5} In _{0.5} P	InAs	Si
AlN	(In,Ga)N	SiC
Al ₂ O ₃	InN	Si ₃ N ₄
AsSG (Arsenosilicate Glass)	InP	SiO ₂
Au	InSb	Si _x O _y N _z
	(In,Sn)	Sn
Bi	(In _x Sn _y)O	SnO ₂
BSG (Borosilicate Glass)	In ₂ Te ₃	
		Ta
C (amorphous)	KTiOPO ₄ (KTP)	TaN
C (Diamond)		Ta ₂ O ₅
(C,H,[O,N,F,Cl,Br])-Polymere	LiAlO ₂	TaSi ₂
CdS	LiGaO ₂	Ta _{0.72} Si _{10.28} N
CdTe	LiNbO ₃	Te
(Co,Cr)		Ti
(Co,Nb,Zr)	Mg	TiN
Co ₂ Si	Mo	TiO ₂
Cr	MoSi ₂	
Cu		V
	Nb	W
Fe (Fe,C)	NbN	WO ₃
(Fe,Ni)	Ni	WSi ₂
	(Ni,Cr)	YBa ₂ Cu ₃ O _{7-x} (YBCO)
GaAs	NiMnSb	
(Ga,In)As		Zn
(Ga _{0.5} In _{0.5} P	Pb	ZnO
GaN	PbS	ZnS
(Ga, Gd) ₂ O ₃	Pb _{0.865} La _{0.09} Zr _{0.65} Ti _{0.35} O ₃	ZnSe
	(PLZT)	

Symbols

A	– area, electrode area
A_B	– etching area
A_{ges}	– total area
A_+	– anodic electrode area
A_-	– cathodic electrode area
a	– chemical activity
a_i	– chemical activity of particle of kind i
B	– percentage area of coverage
$B $	– base, ligand
b	– width of pattern
C, c	– concentration
C_0	– concentration in the interior of the solution
C_{SF}	– concentration at the surface
c_0	– initial concentration
D	– diffusion coefficient
$DS \downarrow$	– precipitate
d	– thickness of diffusion layer
d'	– apparent thickness of diffusion layer
d_g	– limiting diffusion layer thickness
E	– potential
E	– electric field strength
E_0	– normal potential
E_B	– bias field strength
E_f	– floating potential
E_i	– ion energy
e^-	– electron, negative elementary charge
F	– Faraday constant
h	– film thickness, height of structure
h_{etch}	– etch depth
$h_{etch/pass}$	– material removal up to passivation

XII *Symbols*

I – current
 I_+ – anodic current
 I_- – cathodic current
 I_0 – cathodic partial current on large areas in outer-currentless case
 i – current density
 i_+ – anodic current density
 i_- – cathodic current density
 i_0 – cathodic partial current density on large areas in outer-currentless case

K – equilibrium constant
 K_B – complex forming equilibrium constant
 K_L – solubility product
 K_+ – chronopotentiometric constant
 k – constant
 k – Boltzmann constant

L – uncharged ligand
 l – length, width of pattern
 l_u – undercutting

M – metal or semiconductor
 M_w – molar mass, atomic weight
 m – mass
 m – stoichiometric factor
 m_e – electron mass
 m_i – ion mass

N_0 – Avogadro constant
 n – counting variable
 n – mol number

OM – oxidant

P_e – Peclet number
PR- – polymer molecular residue (polymer trunk, polymer radical)

R – gas constant
 $R\cdot, R\cdot$ – radical
 r – etch rate
 r_B – gross etch rate
 r_d – average etch rate
 r_{el} – electrochemical etch rate
 r_h – etch rate of an auxiliary layer
 r_H – horizontal etch rate

r_m	– etch rate of mask
r_n	– etch rate dependent on total area
r_p	– penetration rate (etch rate of interface)
r_{res}	– removal rate of material not to be etched
r_0	– radius of tube reactor
S_{etch}	– etching selectivity
T	– absolute temperature
T_e	– electron temperature
t	– time
t_{etch}	– etching time
t_v	– overetching time
t_0	– etching time up to complete removal of film
V	– volume, plasma volume
v	– velocity
v_0	– gas flow rate in inlet region of an apparatus
v_e	– velocity of energized particles
w	– pattern distance
w_f	– width of sidewall
X^-	– monovalent acid anion, monovalent negative ligand
x	– local coordinate
x	– stoichiometric factor
Y	– ligand, uncharged
y	– stoichiometric factor
Z	– acid radical ion
z	– stoichiometric factor
z	– electrochemical valency
z_+	– anodic electrochemical valency
z_-	– cathodic electrochemical valency
α	– interface angle, slope angle
α_{IF}	– slope angle during preferred etching
α_m	– slope angle of etching mask
β	– reactivity factor in plasma etching
γ	– degree of anisotropy
ϵ	– potential
ϵ_0	– zero-current potential

XIV *Symbols*

- ν – frequency
- ν_i – stoichiometric factor of particle of kind i
- ρ – density (specific mass)
- Σ – sum
- τ – transition time
- τ – life time of reactive plasma species
- t_0 – transition time in outer-currentless state

Abbreviations

ARDE	– Aspect-Ratio-Dependent Etching
AsSG	– Arsenosilicate glass
CAIBE	– Chemical-assisted ion beam etching
EBRE	– Electron-beam-supported reactive ion etching
ECM	– Electrochemical machining
ECR	– Electron cyclotron resonance
EDTA	– Ethylene diamine tetraacetic acid
EMM	– Electrochemical micromachining
ERIBE	– Electron-beam-enhanced reactive ion beam etching
FIB	– Focussed ion beam etching
HF	– High frequency
IBE	– Ion beam etching
IBAE	– Ion-beam-assisted etching
ITO	– Indium tin oxide
JEM	– Jet electrochemical micromachining
KTP	– Potassium titanyl phosphate, potassium titanate phosphate
LPCVD	– Low pressure chemical vapour deposition
M	– Metal, semiconductor
MIE	– Magnetic-field-enhanced ion etching
MERIBE	– Magnetic-field-enhanced reactive ion beam etching
MERIE	– Magnetic-field enhanced reactive ion etching
NA	– Numeric aperture
NPBE	– Nanoparticle beam etching
OM	– Oxidant

XVI *Abbreviations*

m_e	- Electron mass
P_a	- Adsorbed product
P_d	- Desorbed product
PE	- Plasma etching
PEC	- Photoelectrochemical etching
PJE	- Plasma jet etching
PMMA	- Polymethyl methacrylate
PSG	- Phosphosilicate glass
PZLT	- Lead lanthanum zirconate titanate
PZT	- Lead zirconyl titanate, lead zirconate titanate
R	- Radical
RIBE	- Reactive ion beam etching
RIE	- Reactive ion etching
RNE	- Reactive neutral gas etching
rf	- Radio frequency (= HF – High frequency)
SCE	- Saturated calomel electrode
SECM	- Scanning electrochemical microscope
SF	- Surface
T_{en}	- Energized particle
T_r	- Thermalized reactive particle
UME	- Ultramicroelectrode
UV	- Ultraviolet
YBCO	- Yttrium barium cuprate

1 Introduction

Microtechnical patterning methods deal with the preparation and application of components that cannot be prepared by classical mechanical methods. The precise designing of various materials is a quite essential prerequisite for fabricating microdevices. Micropatterning of substrates and films microdevices are composed of, is therefore an elementary process of physical microtechnique.

While cutting methods are essential in precision-mechanical designing they do not play a role in microtechniques. Instead, etching processes are the most essential methods for designing micropatterns. Etching processes in combination with electron beam lithography and, especially, with photolithography have become the central tools of microproduction. Along with a large group of standard methods, in which lithographic masks are used for patterning, a lot of special methods have been developed, partly using masks, partly working without them.

The subject of this book are lithographic etching processes. For a long time etching processes have played an important role in microcrystallographic material analysis. They were developed in semiconductor technology for characterizing semiconductor solid materials. The etching media were optimized to make visible morphological characteristics, e.g., crystallite structure, lattice disturbances or doping boundaries. Some of the methods are used today, either in their original or in a modified form for micropatterning by means of lithography. Those etching methods that serve exclusively to make the texture of solids visible are not considered here.

Although application of etching techniques in microelectronics and microsystem technology was established only in recent years, the combined effect of etching technique and resist technique has been used for a long time. Such aggressive natural liquids like lactic acid, citric acid or acetic acid were probably already used for the treatment of materials in prehistoric times. But only after preparing highly corrosive strong mineral acids (hydrochloric acid, sulfuric acid, nitric acid) by Arabian and European alchemists, systematic treatment of surfaces by etching processes had been possible. During the Middle Ages such etching processes were applied mostly in the field of art and craftwork. Etching of metal surfaces that were partly covered with resins was used largely in the late Middle Ages to adorn arms and armour. The pattern, engraved in the resin, could be transferred permanently into the metal by the

etching process. This kind of metal etching developed into an important means of plastic arts. A metal plate, mostly hammered copper, was covered with a film of varnish. In this film a pattern was engraved by means of a needle. This engraved pattern had to be a negative of the picture, later to be printed. By the following etching process the pattern was transferred into the metal plate in the form of small etched grooves. The width and depth of these grooves depended on the choice of composition of the etch bath or etch paste. After removing the varnish film and applying paint the picture was transferred in a last working step to a paper or another material. Already the Old Masters like Dürer and Rembrandt used this technique of etching.

In opposition to all cutting and engraving methods, the etching technique allowed the fabrication of agreeable patterns without rims, swarf or burrs. With the etching processes in craftwork and in fine arts, where resins are used as resistant films against the etching media, i.e. a resist, we already find the method of the primary pattern generation in the resist and the pattern transfer by local dissolution of a metal which are the essential fabrication steps of the modern microlithographic etching technique.

After the discovery of hydrofluoric acid by Scheele in 1771 the etching of a variety of materials became possible. Hydrofluoric acid was soon used for etching patterns into glass. This was the first time that an inert non-metallic material was designed by an etching process.

A further decisive impuls for the development of the etching method was the discovery that some resins and bitumen hardened under the influence of sunlight (Senebier 1792). This method was used by Nièpce for the storage of pictures (Heliographie, Nièpce 1522). The discoveries of Senebier and Nièpce were applied in manufacturing printing plates of stone. Hence the name lithography for the method from the greek word *lithos* for stone. Transferring photographic images onto stone plates enabled a convenient amplification by printing. A disadvantage was that those images could be transferred in black and white only. Gradation was achieved in 1936 using printing plates with small rasters. The ratio of the width of the raster dots to the etched spaces determines the grey level.

The general principle in all lithographic methods consists in producing a relief by etching through an etch resistant mask. This mask is patterned by engraving a resin or by exposing a so-called photoresist. Thus a two-dimensional shape is determined, its transferring by etching produces the three-dimensional structure, i.e. the relief, in the underlying material. This method has been used on industrial scale since the middle of the 20th century. Already before microscopically small elements had to be fabricated, the etching method proved to be a convenient method for precise shaping of three-dimensional metallic components, especially in the case of workpieces of complex structure. The industrial etching techniques were called *chemical milling*, or *photochemical milling* if the etch mask pattern was generated by exposure to light of short wavelength. The wet chemical etching process has established itself as a special field of the lithographic etching technique in the production of printed circuit boards and integrated solid-state circuitry. Etch-

ing processes developed in microelectronics are now used and adopted in microsystem technology. The rapid growth in the variety of the microdevices demands high reliability and standardization of the devices and great flexibility in technology.

Nowadays etching procedures are applied for a very large amount of materials and a great variety of material combinations in the field of microsystem technology. The majority of metals and semiconductors as well as many alloys and non-metallic compounds are treated by etching processes. The measures of the produced patterns reach from some millimeters to few micrometers in many micromechanical devices. In microelectronics usually structures in the sub-micrometer range (0.5 to 0.3 μm) are produced. By combining electron beam lithography with dry-etching methods structures of less than 0.1 μm , even down to the 10-nm-level can be generated. These structures, however, were used up to now mainly in research only, especially for investigating electronic quantum effects.

Because of the character of the material removal, etching processes are suitable also for extreme miniaturization. With mechanical removal of material, bits of the material are separated. Although these can be very small, they are made up of a lot of atoms or molecules. Whereas in an etching process molecule by molecule or atom by atom is separated from the solid surface. Hence etching processes are of high resolution according to their character. Only with reaching atomic or molecular dimensions, they get to their theoretical border. Therefore etching processes are suited for treating the smallest conceivable solids.

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2 Distinctive Features of Microtechnical Etching

2.1 Etching as a Fashioning Method

As practically in all physically working technologies, the working steps in microtechnology start on a surface. In contrast to precision mechanics working with curved and typically cylindrical surfaces, microtechnology is concerned with flat surfaces mainly. This is explained by the following facts. The building up and removal of material in microtechniques is done by processes reacting on a large area simultaneously, but homogeneously on flat surfaces only, whereas in precision mechanics a special tool works on a single local point at one time. Furthermore, a quite even surface of the solid to be worked, is the precondition for the generation of patterns in the etch-resistant mask by a reproducing lithographic method. Another important difference to cutting and remodelling procedures concerns the character of the process. Even in producing swarf, the removed material is the same in its material properties as the starting material. In etching procedures the removing proceeds by the transition of single atoms or molecules or of small clusters with less than 100 atoms from the solid into a mobile phase. The transition is connected with a material change, at least with the phase transition, mostly, however, with chemical changes. The transport of material from a solid through a phase boundary into a mobile phase is the central characteristics of all etching processes.

Patterns in microtechniques are generated by means of masks mostly. For that purpose a masking layer is prepared on the surface of the work piece, which is called substrate subsequently. The thickness of this masking film lies between some hundred nanometers and a few micrometers. Preferentially, a thickness about 1 μm is used. The masking layer is patterned by microlithographic methods, i.e., it is removed at certain parts and preserved in others. The geometric measures of these patterns in the masking layer correspond to the measures of the devices being produced in the substrate. They are in the order of magnitude from millimeters down to sub-micrometers. According to the kind of pattern transfer one has to distinguish photolithography (using visible light and a photosensitive resist as masking layer), UV-lithography (using UV-light with the resist), X-ray and electron beam lithography (using X-rays or electrons of high energy, respectively, with a special resist as masking

layer). The transfer of the original pattern into the masking layer is feasible on flat surfaces only with most lithographic methods. Thus the tolerance level of flatness is less than 1 μm for ULSI-circuits in photolithography.

2.2.1 Limits of Additive Microtechnical Pattern Generation

Patterning is also possible by local deposition of material on a substrate surface. This technique is called additive patterning. Limiting preconditions exist for additive patterning. If – as usual in microtechniques – the material layers are deposited on the whole substrate area, the additive pattern generation needs masking as well.

E.g., a metal can be deposited locally by a microgalvanic method into openings patterned in an insulating layer on a conductive substrate. In this case the preconditions are electrically conductive and insulating materials, respectively.

The so called lift-off technique is another additive method. A substrate is covered with a mask pattern reverse to the desired functional pattern. The functional film is deposited on this pattern. Subsequently the mask material is dissolved in an appropriate medium and the adherent functional film is lifted off. Only the unmasked areas of the patterns stay covered with the functional material. One precondition in this process is that the side slopes of the mask patterns are not covered with the functional material so that the dissolving medium can get in contact with and attack the mask material. Another is a not too large area to be lifted, because otherwise the dissolution process takes a long time or comes to a standstill. The geometries are dependent on the actual materials used. Furthermore the functional material is not dissolved and chip-pings of it contaminate the solution, eventually disturbing following processing.

Because of the limiting conditions of the additive processes, they play only a minor role in microlithographic patterning.

2.1.2 Subtractive Pattern Generation

Processes in which parts of a complete functional material are removed are called subtractive methods. Subtractive patterning is feasible by a probe technique removing the material directly at a local spot, or by using a mask that protects the areas not to be removed from the general attack of the etching medium.

This mask is generated normally using data recording. The data record can either be used to generate the pattern directly in the etch resistant mask material, the photoresist or electron beam resist, on the respective substrate by means of a so-called photolithographic pattern generator or an electron beam exposure system, or by transferring the pattern from a photolithographic mask, generated by the said methods, in a photolithographic exposure step

with an aligner instrument to the mask material, the photoresist. In both cases the exposed pattern has to be “developed”, i.e., either the exposed or the unexposed part of the pattern will be dissolved, leading to a positive or negative image of the pattern of the applied photolithographic mask, or of the data of the generated pattern, respectively. The development procedure is dependent on the character of the used resist.

In the subtractive working mask processes, the mask produced in the primary pattern transfer step covers all parts of the surface of functional material, which shall remain unchanged. All methods of subtractive pattern generation in a functional material by means of a micropatterned etch-resistant mask material belong to the microtechnical etching methods.

In principle all materials can be patterned by etching processes. Hence microtechnical etching, in opposition to additive pattern generation, is a universally applicable method. The choice of the respective etching process has to be done, however, considering the chemical properties of the materials to be removed and all the other materials not to be removed, but lying open to the etching medium. The etching process not only determines the rate of dissolution of the respective materials, but also affects the geometries, i.e., certain deviations from the pattern of the etch-resistant mask. The rate and selectivity of the dissolution as well as the geometries produced during progressing etching are the essential criteria in choosing the etching procedure.

Etching processes are divided into two major groups, the so-called wet-etching and dry-etching processes (fig. 2-1). The processes of the two groups differ in the mobile phase acting as etching medium, i.e., the phase in which the particles from the solid are transferred into and removed from the surface.

In wet etching processes the detaching of the material is done by its interaction with a liquid, the “etching bath”. The interaction is accomplished by redox and solvation processes. If the oxidation proceeds without an outer source of current, we speak of outer-currentless etching processes. We also know electrochemical, photochemical and photoelectrochemical etching processes with either a source of current, or supported by light or with both. Wet chemical etching processes are classified also by the etch grooves they produce. Generally wet etchants work isotropically, but there are as well wet chemical etchants with crystallographic preferences that work anisotropically. These are used for shaping monocrystalline materials.

In dry-etching methods the material is transferred into the gaseous phase. Along with the etching in reactive vapours, plasma and ion etching processes are of importance. Etching processes working with accelerated ions are subdivided into sputter etching, reactive ion etching and various ion beam etching techniques. Beside the accelerated ions, other sources for activating etching processes in the gaseous phase are used, e.g. electron beams or light.

A separate branch of the microtechnical etching evolved with micromechanics. The term micromechanics is used with two different meanings. On the one hand it stands for the field of miniaturized devices and on the other it includes all those methods that are convenient for patterning and shaping in the microrange with depths that are deeper than those in thin film technology,

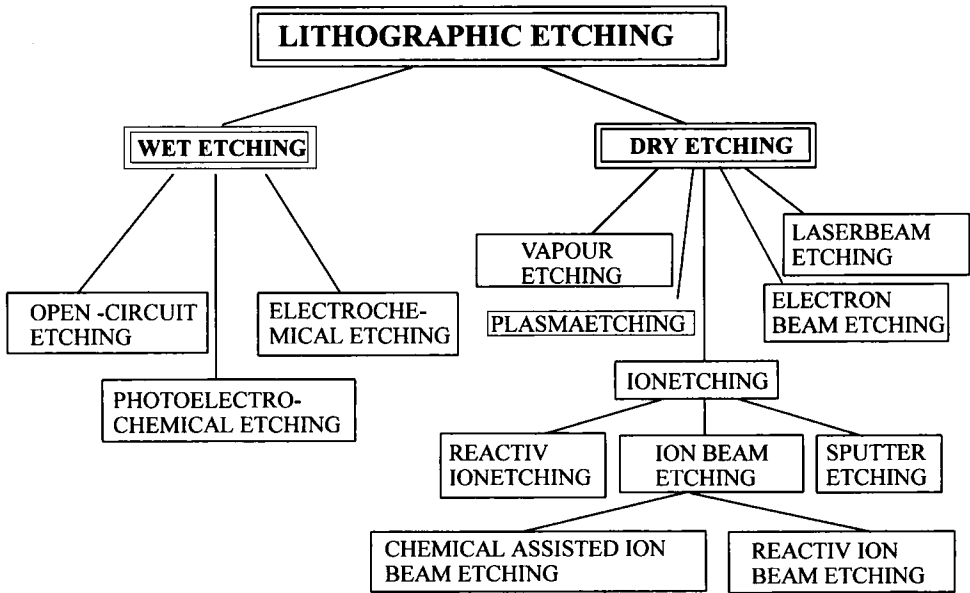


Fig. 2-1. Overview over the most important classes of microlithographic etching processes

i.e. deeper than a few micrometers, and especially, for fabricating flexible microstructures. Also in this field of micromechanics etching techniques are of decisive importance. They dominate over miniaturized cutting methods. The etching methods of micromechanics are distinguished by the etched material and the etch depth as surface and bulk (substrate) micromechanics.

All etching processes have some criteria in common, that are independent of the material to be etched, the kind of etching medium and the application. The important parameters etching rate and selectivity, the form determining parameters degree of anisotropy and degree of sloping of sidewalls decide on the efficiency and quality of an etching process. These parameters shall be introduced in the following, before dealing with the respective groups of methods.

2.2 Etch Rate and Selectivity

2.2.1 Etch Rate and Time Request

Microtechnical etching has to be realized in a technically reasonable time. The various steps of a process should proceed rapidly ensuring a short time required for the fabrication of the whole component. Thus the etching steps should demand times comparable to the other process steps. The times of the photoresist steps have time intervals of some seconds to a minute. With wet chemical processes, this magnitude can be met by choosing a convenient etching medium and etching conditions as long as thin films are to be etched (thickness about $1\ \mu\text{m}$ or less). With thicker films and principally in dry etching processes there are fundamental physical and chemical limits.

Processes at the phase boundary and transport processes from and to the phase boundary cannot proceed with arbitrary velocity. Hence the etching of film and substrate materials with thicknesses of more than $10\ \mu\text{m}$, as e.g. in deep etching of substrates with etching depth of $10\ \mu\text{m}$ to $1\ \text{mm}$, costs more time. Also dry etching processes are of longer duration, as their etching rates often do not exceed 1 to $10\ \text{nm/s}$, sometimes they are even less than $1\ \text{nm/s}$. Thus the etching of a $1\ \mu\text{m}$ thick film needs about 3 to 30 minutes.

With thin films of a few nanometers thickness, etching times much less than a minute can be achieved. However, ensuring good controllability and reproducibility of the etching process the etching time must not be too short, as the starting and the end phase of etching are especially prone to interferences. The quality of an etching process is difficult to control if the actual etching process is of short duration in comparison to its initial and end phase, e.g. the removal of contaminating films, the immersion and taking out of the substrate or the switching on and off of a plasma influence the beginning and the end. Because of this etching times of about 1 minute are to be preferred.

2.2.2 The Etching Process

In contrast to high precision and ultra high precision mechanics in microtechnical etching the material is transferred in form of single atoms or molecules from the solid into the liquid or gaseous phase (mobile phases). Each etching process, therefore, is a process in which material is transferred through a phase boundary. Because of the removal of single atoms or molecules in the elementary steps, very high accuracies can be achieved. The elementary process of etching becomes limiting only on the molecular or atomic scale for the accuracy of patterning.

The central physical quantity for subtractive patterning in a material to be treated microtechnically is the etch rate r . It is the ratio of the actual etched material thickness h_{etch} and actual etching time t_{etch} .

$$r = h_{\text{etch}} / t_{\text{etch}} \quad (1)$$

The etch rate also can be given as an average (medium) etch rate r_m for the etching of the whole film of the thickness h , where the end of the etching process is defined by the disappearing of the film after the etching time t_0

$$r_m = h / t_0 \quad (2)$$

The temporary etch rate $r(t)$ deviates often to a great extent from the medium etch rate r_m . It is determined by the differential quotient of film thickness and time.

$$r(t) = dh / dt \quad (3)$$

The transfer through the phase boundary is understood as a pure physical process only, if atoms or molecules are detached directly by a mechanical impuls. That, however, is the case only in detaching solid material by an exclusively mechanical effect of particles of high energy (sputter effect – see section 4.4.1). But also in this case, as in all other cases, the detachment of the atomic or molecular particles from the surface is connected with a change in the interaction of the particles within the surface, i.e. their mutual acting cohesive and chemical bonds.

Except for the sputter effect, the chemical component dominates nearly all etching processes in the actual step of phase transition. During etching as well in liquid as in gaseous media, the particles of the mobile phase interact with those on the surface causing them to leave the solid. In the molecular or atomic environment the neighbouring atoms or molecules of the detached surface particles are substituted by particles of the mobile phase or the interaction among the surface particles is minimized transferring the surface particle or its reaction product by thermal activation spontaneously into the mobile phase. In wet chemical etching processes the change in the interaction in the neighbourhood of the particle is accompanied by a chemical change, e.g. the building up of a shell of solvent molecules (solvation), or of ligands (complexing), the transition of charge (redox reaction), or a combination of these processes.

2.2.3 Transport Processes

The transport of the particles from the interface into the interior of the mobile phase is of physical nature. Either it is caused as an oriented movement by momentum transfer (etching processes in vacuum) or by brownian movement in a concentration gradient (diffusion). With momentum transfer by energized particles the rate of the etching process is independent of the velocity of the movement of the single particle from the surface. The etching rate is determined in this case by the number of impacting energized particles and the number of detached particles of the solid per impacting particle.

Transport by diffusion is the quicker the greater the difference of concentration per unit of length (concentration gradient), i.e. diffusion-controlled etching processes possess etching rates that are the higher the greater the molecular mobility of the particles to be transported, the higher their concentration on the surface of the solid, the lower their concentration in the interior of the mobile phase, and the shorter the distance between the solid surface and the interior of the mobile phase (diffusion distance).

The transport process can be accelerated by a spontaneous or forced movement in the mobile phase (convection). This accelerating effect is caused by a relative motion of the solid surface to the near-surface area of the fluid phase that increases the concentration gradient and thus improves diffusion. In special cases transporting is supported by a field, e.g. electrical migration.

In all dissolution processes in a liquid medium, but also in etching processes in a reactive plasma the reaction at the phase boundary is preceded by a transport process of the reactants from the mobile phase. The atoms and molecules, necessary for the phase transition, have to move from the interior of the liquid phase to the solid surface where they react. If the passage of energized particles to the surface, of which particles have to be sputtered off, is considered as a transport process as well, it applies for all etching processes that the actual phase transition step is preceded by an transporting step to the surface. Thus results the general division in three steps of the etching process:

1. Transport of the reacting particles from the interior of the mobile phase to the solid surface
2. Transition at the solid surface
3. Transport of the detached particles from the solid surface into the interior of the mobile phase.

2.2.4 Process Velocities

As the above mentioned three general steps of the etching process are succeeding steps, the velocity of the etching process is determined by the slowest step. Thus we differentiate between transport-controlled and interface-controlled etching processes. The transport controll can be caused by the transport of the reactants to the solid surface or the transport of the reaction products off the solid surface. Diffusion-controlled etching processes play a decisive role in many wet etching processes.

The transport controll by diffusion is described by the 1. Fickian Law:

$$dc/dt = D \cdot dc/dx \quad (4)$$

The transport of matter is given by the change of concentration in time (dc/dt). This change is the quicker the higher the specific diffusion constant (D) and the local concentration gradient (dc/dx). Under most hydrodynamic conditions a diffusion layer of a characteristic thickness is formed in the vicinity of

the solid surface. In this layer the transport is determined by diffusion, exclusively. Outside the layer, convection contributes largely to the material transport. Under stationary conditions, i.e. with a constant flow of matter in the diffusion layer, the concentration gradient is temporally and locally constant. In this case the concentration gradient equals the quotient of the difference of the concentration in the interior of the solution C_0 and the concentration at the interface C_{SF} and the thickness of the diffusion layer d :

$$dc/dx = (C_0 - C_{SF})/d \quad (5)$$

If the transport of reactants to the surface is the controlling step, a higher etching rate is achieved by increasing the concentration of the limiting species in the solution. If the rate is controlled by the diffusion of the reaction products from the surface, the concentration of those should be small in the interior of the solution.

Equation (5) shows that the transport process can be accelerated efficiently by reducing the thickness of the diffusion layer, as the concentration gradient increases with decreasing diffusion layer thickness at the same concentration difference and with that the diffusion rate (eq.(4)). The thickness of the diffusion layer depends on the viscosity of the solution and the convection in the solution. With increasing convection the diffusion layer thickness is reduced. Therefore, transport-controlled etching processes are accelerated by moving the substrate in the etching medium, by stirring the etching medium, by ultrasonic treatment and other convection intensifying measures. Working with a rapidly spinning substrate and spraying the etch medium through nozzles on it is an effective method. According to the Levic equation the diffusion layer thickness at a rotating disc decreases in dependence on the square root of the spinning velocity ω :

$$d = k \cdot 1/\sqrt{\omega} \quad (6)$$

Without any forced convection the diffusion layer thicknesses are between about 50 and 500 μm , typically¹. These values result from the spontaneous convection in liquids caused by slight temperature and density gradients. In open etching baths these gradients occur because of the cooling by evaporation at the liquid surface. Etching processes are in the most cases exothermal processes and thus the dissolution itself contributes to the formation of minor temperature gradients responsible for spontaneous convection.

In dissolution processes the density of the solution near to the dissolving surface is changed because of the changing in chemical composition. The occurring density difference contributes distinctly to the spontaneous convection and therefore diminishes the diffusion layer thickness. Convections caused by the reaction process can diminish the diffusion layer thickness to

¹ K. Vetter (1962)