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Tutorial

Laser in material nanoprocesing

1 Introduction

The American engineer and physicist Dr. Theodore “Ted” Harold Maiman invented the first working laser on May 16, 1960. The journal Physical Review Letters rejected his manuscript but Nature finally published the paper on August 6 the same year [1]. He received a US patent for his invention on Nov 14, 1967 [2].

The first laser was a ruby laser emitting in the red spectral region at 694.3 nm. This novel artificial light source, which provided intense coherent radiation, opened up completely new technologies and applications such as the introduction of nonlinear optics. The theoretical basis of two-photon technology was provided by the PhD student Maria Göppert in 1929 [3], but at that “pre-laser” time, there was no light source to prove her hypothesis of two-quantum transitions. In 1961, shortly after Maiman’s invention, second harmonic generation (SHG) and two-photon excited fluorescence were demonstrated [4, 5]. Nonlinear optics was born. The simultaneous absorption of multiple photons resulted in multiphoton ionization, optical breakdown, and plasma formation.

Also in 1961, the first laser radiation effects on eyes were studied using live rabbits [6–8]. Somewhat later a ruby laser was employed to destroy a retinal eye tumor in humans. Goldman reported on the pathology of the effect of laser beams on skin [9, 10]. Laser medicine began.

In 1962, Brech and Cross achieved a ruby laser induced microemission of materials and introduced laser-induced breakdown spectroscopy (LIBS) [11]. In the same year, the LIBS instrument was commercialized as Laser Microprobe by the US company Jarrell-Ash. An advanced laser microscope, LMA 1 (laser micro analyzer), was developed by VEB Carl Zeiss Jena in 1964. One year later, Birnbaum observed laser-induced periodic surface structures (LIPSS) in semiconductors, also termed ripples, with a periodicity close to the exposure wavelength [12].

At that time, several other laser types had been invented. The first semiconductor laser was realized in 1961, the HeNe laser in 1962, the CO₂ laser (10.6 μm), the Nd:YAG laser (1064 nm), and the dye laser in 1964. The laser printer was invented in 1973. One year later, the barcode scanner was introduced.

A major step was the invention of the excimer laser. Now a powerful ultraviolet (UV) laser source with a wavelength of 308 nm and shorter became available. Nanoprocessing, meaning the fabrication of feature sizes below 100 nm, was now realistic. Two major applications of the excimer laser in the field of material processing
today are photolithography for the integrated circuit (IC) industry and the shaping of the human cornea for the treatment of shortsightedness, a technique called LASIK.

In addition to the availability of short wavelength laser sources, a further important technological step for the realization of material nanoprocessing occurred. In particular, bulk nanoprocessing became possible with the generation of ultrashort laser pulses. As shown in this book, even the use of long wavelength infrared radiation enables nanoprocessing when femtosecond lasers are employed.

“Conventional” lasers such as the ruby and excimer laser typically operate with nanosecond or even longer pulses. For the first time, pulses in the picosecond-range were generated by passive mode-locking of a ruby laser in 1965 [13].

The first femtosecond laser was realized in 1976 using dye lasers [14]. In 1981, the first sub-100 fs laser pulse was generated [15]. Using a mode-locked femtosecond dye laser, the first two-photon femtosecond laser scanning microscope was introduced in 1990 [16]. At that time, the solid state mode-locked Titanium:sapphire lasers with a spectral bandwidth of more than 200 nm began to replace the femtosecond dye laser systems [17].

Using ultrashort laser pulses can cause the ablation of the surface as well as in bulk areas of many kinds of materials, leading to very precise machining results with minimal damage to the micro-environment and even nano-environment. This includes even the nanomachining of delicate materials with high heat conductivities or comparatively low melting temperatures, such as metals, as well as optically transparent non-organic and organic materials such as cells and tissues. This book focuses mainly on the use of long wavelength ultrashort laser pulses for nanoprocessing.

2 Laser-material interactions

Most laser-material interactions are based on linear or nonlinear absorption. Exceptions are reflection, scattering, diffraction, and other forms of changes of the photon direction. In fact, these changes are employed in optical coherence tomography (OCT), SHG microscopy, and optical trapping, where the change of momentum results in optical forces. Depending on the interaction of photons with atoms or molecules of the materials, light can be scattered elastically or inelastically. In elastic light scattering processes, e.g. Rayleigh scattering, the scattered light exhibits the same wavelength as the incident light, whereas in inelastic scattering, e.g. in Raman scattering, the frequency of the scattered light is shifted towards a higher or lower value.

One-photon absorption takes place along the beam path depending on the spectral absorption behavior. Selective absorption of the spectrum is the origin of the color of many optical materials. If a crystal appears red, this can be attributed to the absorption of the complementary colors blue and green. All materials absorb UV light due to absorption by bound electrons. Typically, the UV laser beam has a low light penetration depth of some micrometers. Luminescence can be observed in many types
of materials along with absorption. Luminescence, which is a spontaneous emission process, occurs if a material is transferred prior to the emission to an excited state. Luminescence light can be emitted in all directions, its frequency is usually different from the excitation frequency. Depending on whether a spin change of the electronic state is involved, luminescence can occur either as fluorescence or phosphorescence, the latter accompanied by a change of the total spin.

In contrast to linear or single-photon absorption, multiphoton absorption depends strongly on the applied light intensity. For many transparent materials, the intensity of the visible or near infrared laser beam has to be on the order of GW/cm² (10⁹ W/cm²) in order to achieve multiphoton absorption. Therefore, nonlinear absorption is induced most efficiently only in the center of a small laser spot of a tightly focused laser beam. This allows for sub-100 nm processing even when the laser spot size is about half a micrometer.

Typically, small laser spots are required in single-photon and multiphoton nano-processing. According to Ernst Abbe’s famous diffraction formula (Fig. 1), the spot size $d$ of a “perfect” laser beam such as a Gaussian beam depends on the wavelength and numerical aperture (NA) of the focusing optics. NA is defined as the product of the refractive index of the environment, such as 1.00 for air, times the sinus of half the incident beam angle after transmission through the optics. This means that the typical minimum spot size $d$ for non-UV radiation is about 200 nm.

$$d = \frac{\lambda}{2 \cdot NA}$$

For a spatial profile of a laser beam with different TE-modes, the minimum spot size $d$ can be calculated according to

$$d = \frac{2 \cdot M^2 \cdot \lambda}{\pi \cdot NA}.$$  

Different methods can therefore be applied in order to achieve a small laser spot size: A laser system with good spatial beam quality can be chosen ($M^2$ close to 1.0; $M^2$ is defined as the beam parameter product divided by the corresponding product for a diffraction-limited Gaussian beam, with the beam parameter product as the product of focal radius and far field divergence angle), but also a short wavelength $\lambda$ or a high NA which can be as high as 1.5, when using special immersion oil objectives. High NA values imply a short working distance.

Recent developments in the field of laser sources have led to lasers with excellent beam quality, also in the UV spectral range. Besides spatial optimization, also temporal measures can be taken to influence the intensity of laser radiation and the duration of the interaction between laser and material. Using pulsed lasers, the peak power can reach multiple orders of magnitude higher values, than the average power.

An illustrative overview is provided in Fig. 2, where state-of-the-art laser systems are classified according to their pulse peak power and pulse duration.
Fig. 1: Photograph of a sculpture with Abbe’s famous formula in the city of Jena, where Ernst Abbe worked as university professor and later as director of the ZEISS factory.

Fig. 2: Lasers for micro- and nanoprocessing classified according to their temporal pulse length and peak power.

3 UV laser nanoprocessing

According to conventional (linear) optics and Abbe’s law, there are some established methods for shifting the diffraction limit to smaller structure sizes. A mature technology is optical lithography using UV laser radiation, i.e. making use of the linear scaling of the resolution limit with the exposure wavelength. Optical lithography is the standard manufacturing technology in the semiconductor industry and has been further developed during the last five decades to allow minimum structure sizes far below the micrometer range. This technology has been driven by the demand of higher transistor and integration density of microprocessors and storage components. Figure 3 depicts the development of microprocessors during the last 40 years. Gordon Moore, one of the founders of computer processor giant Intel\textsuperscript{®}, postulated exponential growth (every
Moore’s Law

Fig. 3: “Moores’ Law” was predicted by the co-founder of Intel®️, Gordon Moore, in 1965 and slightly corrected in 1975. The graph shows its validity until today.

18 months the complexity of integrated circuits will be doubled) and his forecast has turned out to be pretty correct so far.

The common technology of optical lithography is based on the transfer of a mask pattern by an optical system onto a semiconductor substrate. Silicon substrates coated by a thin resin material are mostly employed in microelectronics. The resin is modified by UV radiation and acts as a resist material for etching processes, after it has been developed. The performance of optical lithography can be impressively demonstrated by the latest generation of nanoprocessors, where minimum structure sizes of 22 nm on wafer diameters of 300 mm are realized (Fig. 4). Additional optical and chemical effects have been explored in order to achieve such small structures when applying an ArF excimer laser at 193 nm. Figure 5 shows the different processing steps in the semiconductor industry.

The surface which is going to be structured, is initially coated by a radiation sensitive thin resin (photoresist). Different photoresists, based on either polymers or epoxy resins, can be used. In order to enhance the photochemical reaction, additional photosensitive molecules are mixed into the resin. In negative tone resist materials the solubility for the developer is decreased on illumination with UV-radiation. Weak $\pi$-bonds between the resist molecules are transferred into strong intermolecular $\sigma$-bonds. In contrast, in positive tone materials, the solubility is increased. In this case the resist material has been solidified during thermal pretreatment. The UV-radiation then breaks the bonds and, as a consequence, increases solubility in the subsequent development process. Positive resists are usually made up of three components: (i) a resin which is readily soluble in an alkaline developer (often novolak); (ii) a photoactive component (often diazonaphthoquinone, in short: DNQ), which ensures that the resin in the unexposed state is insoluble; and (iii) the solvent (often esters from alcohols and carboxylic acids), which makes the resin flowable.
Fig. 4: 3D field effect transistors with 32 nm structure sizes (a) and 22 nm structure sizes (b) manufactured by double pattern UV immersion lithography. Source: Intel Inc. (left Sandy Bridge, right Ivy Bridge).

The exposure is typically realized by mask projection, while the mask is composed of a chrome-on-glass setup. The choice of positive or negative tone lithography is determined by the type of structure. The larger the area of the mask covered by chrome, the smaller the scattering will be in the beam guiding system. If only small single structures (e.g. micro-vias) have to be processed, positive tone materials are preferably used. On the contrary, if only single structures have to be generated, negative tone resists offer some advantages. After the essential processing step (etching for geometrical structures, doping for the generation of different semiconductor properties, coating of thin layer structures), the remaining photoresist material is finally stripped off.
In addition to the resin properties and related chemical processes, the exposure setup is of crucial importance for the result. Ideal structures are obtained only at a controlled and uniform illumination. Basically, three exposure variations (Fig. 6) can be distinguished: contact exposure, proximity exposure, and projection exposure.

In the case of contact exposure, the mask is “pressed” by vacuum directly onto the coated wafers covering the entire wafer surface. During exposure, the structures are transferred to the photoresist by a scale of 1:1. Since both the chromium pattern on the mask substrate and the photoresist layer are very thin, near field diffraction of the light can occur on the edges of the chrome patterns. The contrast between exposed and unexposed areas is very high using this method. The problem with this form of exposure is the need to push the bottom of the mask with the chromium into the soft resist structure. This problem can be overcome by proximity exposure, in which the mask is placed at a small distance above the wafer surface. However, this decreases the resolution and contrast, since diffracted light can penetrate the gap between wafer and mask. The more complex and expensive mask projection is used for larger quantities and smaller structures. The lower the structure size, the more complex the production of 1:1 masks is. Even the slightest error in mask production is accurately transferred. In mask projection the masks are transferred for example on a scale of 5:1. This reduces mask production, costs significantly. Such illumination tools often operate in the step-and-repeat mode, i.e. not the entire wafer is uniformly illuminated but only a small field, which then, gradually strung together, covers the entire wafer. To minimize chromatic aberrations and absorption effects, small, modern mask projectors are often designed based on reflective optics. When using a UV laser with a narrow linewidth as an illumination device, perfectly crafted lenses can be used. Today, modern mask projection with an ArF laser at 193 nm is often used.
4 Femtosecond laser technology

Alternative to the use of UV laser radiation, very short pulses are able to effectively reduce structure sizes by their unique interaction with materials. The short interaction time in conjunction with extremely high intensities in the focal area, can induce nonlinear absorption for example. The general method for generating ultrashort laser pulses with pulse duration in the ps- to fs-range, is mode-locking. Pulses in the ps-range were generated for the first time by passive mode-locking of a ruby laser shortly after its discovery [13].

Mode-locking can be effectively realized for laser media with a relatively broad laser transition bandwidth and thus, for lasers with a broad amplification profile, in which numerous longitudinal modes can oscillate simultaneously. Assuming that $2N + 1$ modes oscillate with the same amplitude $E_0$ and a constant phase relation between the modes, the resultant field amplitude $E_{\text{tot}}(t)$ can be expressed as a function of the time $t$:

$$E_{\text{tot}} = E_0 \sum_{n=-N}^{N} e^{2\pi i[(v_0 + n\Delta v_{n,n+1})t + n\phi]} ,$$

with the central mode frequency $v_0$ and the phase difference $\phi$, while the frequency distance between two neighboring longitudinal modes $\Delta v_{n,n+1}$ is given by

$$\Delta v_{n,n+1} = \frac{c}{2L}$$

since the resonator length $L$ must be an integer multiple of half the wavelength. It is assumed that at $t = 0$ all modes fulfill the phase condition. Due to their different frequencies, they leave the phase condition immediately after this point in time. However, constant phase relation occurs at periodic time intervals, where the frequency distance is an integer of the inverse cycle time of the resonator. At these points in time, all modes are at their field maximum, so that the superposition of the $2N + 1$ modes reaches its highest theoretical value $(2N + 1)E_0$. In the case of uncorrelated modes, this value would never be reached.

The resultant total irradiance $I_{\text{tot}}(t)$ is given by:

$$I_{\text{tot}}(t) = I_0 \left| \frac{\sin [(2N + 1) \cdot (2\pi \Delta v_{n,n+1}t + \phi)/2]}{\sin [(2\pi \Delta v_{n,n+1}t + \phi)/2]} \right|^2$$

The superposition of the single modes with a constant phase difference leads to laser pulses with a duration $\tau_p$

$$\tau_p = \frac{1}{2N + 1} \frac{1}{\Delta v_{n,n+1}}$$

and a temporal distance between the laser pulses $\Delta t_p$

$$\Delta t_p = \frac{2L}{c}$$
The peak intensity $I_p$ of the single pulses is given by:

$$I_p = (2N + 1)^2 I_0.$$ 

Thus, the peak intensity is $(2N + 1)$ times the sum of the single intensities when the oscillating modes are statistically coupled. In order to achieve phase coupling between the oscillating modes, different methods can be applied within the laser resonator. They are subdivided into active and passive mode-locking techniques.

**Active mode-locking**

Active mode-locking implies that the resonator is equipped with a modulator close to one of the resonator mirrors. The modulator is triggered by an external signal in such a way that a sinusoidal modulation of the losses or the optical path in the optical resonator takes place with a frequency $d\nu$. The frequency $d\nu$ is equal to the frequency difference $\Delta \nu_{n,n+1}$ of the longitudinal modes. Initially, this loss modulation represents an amplitude modulation AM with the frequency $d\nu$ of the mode which starts to oscillate first at a maximum amplification at the frequency $\nu_0$. This modulation then induces the neighboring modes with the frequencies $\nu_0 \pm d\nu$, which experience an amplitude modulation as well. This process continues until all longitudinal modes within the amplification bandwidth of the laser are coupled and synchronized. The induction of the side bands automatically results in the constant phase relation.

When observing this phenomenon in the time domain instead of the frequency domain, the modulation frequency $d\nu$ would correspond to the time period $T = 2L/c$, which in turn corresponds to a full cycle inside the resonator. Thus, from a temporal point of view, the electromagnetic waves passing inside the resonator keep coming across the same modulation cycle. This means that all parts of the wave are attenuated, except for the part which passes the modulator just in the exact moment in which the loss is just about 0. Therefore, short-pulsed radiation concentrates in the time regions with minimum modulation losses. A similar situation arises when modulation of the refractive index takes place instead of attenuation. By changing the refractive index, the optical path is modified. Active mode-locking can be used not only in pulsed lasers, but also in cw-lasers [18]. Generally, electro-optic and acousto-optic modulators can be used in both cases.

**Passive mode-locking**

Passive mode-locking is based on the same principle as active mode-locking, that is a temporal modulation of the resonator losses. In contrast to active mode-locking, the laser system itself determines the point in time at which the losses are at their minimum [19]. The loss modulation takes place either by means of an intensity dependent
absorption caused by a saturable absorber [20] or the use of the Kerr effect [21]. Due to the fact that many modes oscillate simultaneously in an oscillator with a broad amplification bandwidth, the intensity initially shows a statistic temporal behaviour. Such time dependent intensity automatically causes a temporal loss modulation in the absorber. This gradually leads to an arrangement with a constant phase relation between the individual longitudinal modes.

In passive mode-locking using saturable absorbers, mode-locking starts from normal noise fluctuations in the laser cavity. Once a noise spike exceeds the threshold of saturating an absorber, the losses decrease, and gain increases in the round trip. The thus initiated spike begins to grow, and becomes shorter, until a stable pulse width is obtained. The advantage of this setup is that the reflected front edge of the pulse and the approaching back edge of the pulse interfere inside the absorber, which results in saturation at lower intensities. For the generation of ultrashort laser pulses in solid-state lasers currently Kerr lens mode-locking is usually applied. This method uses the nonlinear Kerr effect, i.e. the dependency of the refractive index on incident intensity

\[ n = n_0 + n_2 \cdot I. \]

If a laser beam with high intensity and Gaussian profile passes a Kerr medium, the refractive index is not spatially constant due to the intensity profile. According to the high intensities close to the center of the laser beam, the refractive index and, accordingly, the optical path is higher than in the outer regions. Consequently, the Kerr medium acts as a gradient index lens (Kerr lens). For Kerr lens mode-locking, an aperture is installed in the focal point of the Kerr lens. The focused pulsed beam passes through while most of the low intensity radiation (Fig. 7) is blocked. This intracavity aperture enables the mode-locked pulses with high intensities to pass through and blocks the modes with statistical phase relation and low intensity level until they get the right phase relation by accident.

**Fig. 7:** Principle of Kerr lens mode-locking. The figure on the left represents the low intensity regime. The figure on the right becomes valid for high intensities.
5 Multiphoton effects

Multiphoton effects were predicted by the young PhD student and later Nobel Prize winner for physics, Maria Goeppert in 1929 [3]. Her theory was proven in 1961.

Figure 8 demonstrates the principles of two-photon excited fluorescence, two-photon photochemistry, and multiphoton ionization.

Two-photon fluorescence applies typically two NIR photons at twice the wavelength normally required to excite the visible fluorescence. Because two-photon absorption spectra are broad, the excitation with a fs laser beam at a certain wavelength in the range of 700 to 1200 nm results in the excitation of a variety of fluorophores. Note that a 10 fs laser beam covers a wavelength range of about 100 nm.

Fig. 8: Two-photon excited fluorescence, two-photon photochemistry, and multiphoton ionization.

Two-photon fluorescence is mainly employed in the laser microscopes of cell biologists and neurobiologists. Non-amplified 100-fs NIR laser resonators at a high repetition frequency of 80 MHz with mean in situ powers of 1–50 mW and transient GW/cm² light intensities at the sample, are typically employed.

Note that, in principle, two-photon effects can be generated even with highly focused cw-laser beams such as those used as optical traps with powers of some hundred milliwatts [22]. However, the use of femtosecond laser pulses is by far more efficient due to the high “transient” peak power and a typical low beam dwell time of some microseconds per pixel for fluorescence photon collection, in laser scanning microscopes.
With special long-working distance objectives, a long-wavelength NIR excitation, and clearing agents, deep-tissue imaging of several millimeters has been performed in the brains of live mice.

Two-photon and three-photon chemistry have been realized based on photooxidation processes from the long-lived triplet state to induce photodynamic reactions in biological tissues and cells. For photolithography, conventional photoresists such as SU-8 can be easily employed and “photoactivated” by intense visible and NIR laser beams.

When using high intensities such as TW/cm², four or more photons can be absorbed simultaneously, resulting in the generation of free electrons from the material. Multiphoton ionization occurs. When a certain density of free electrons is exceeded, plasma is generated. When using a liquid microenvironment, plasma-filled cavitation-bubbles can be observed. Furthermore, shock waves are generated. Destructive effects based on cavitation bubble dynamics and shock wave generation are termed photodisruptive effects. Photodisruptive effects scale with pulse energy. In order to avoid collateral effects, the lowest pulse energy possible should be employed for nanoprocesing.

6 Laser-matter interactions for ultrashort laser pulses

Laser ablation is the removal of material from a substrate by direct absorption of laser energy. The onset of ablation occurs above a threshold fluence, which depends on the absorption mechanism, particular material properties, surface structure, morphology, the presence of defects inside the material, and on laser parameters such as wavelength and pulse duration. Typical threshold fluences for metals are between 1 and 10 J/cm², for inorganic insulators between 0.5 and 2 J/cm² and for organic materials between 0.1 and 1 J/cm². The threshold may decrease with multiple pulses due to accumulations of defects. Above the ablation threshold, the thickness or volume of material removed per pulse, typically shows a logarithmic increase with fluence.

A variety of mechanisms for material removal may be involved in laser ablation processes, depending on the particular material system and laser processing parameters such as wavelength, fluence, and pulse length. At low fluences, photothermal mechanisms for ablation include material evaporation and sublimation. For multi-component systems, the more volatile species may be depleted more rapidly by changing the chemical composition of the remaining material. With higher fluence, heterogeneous nucleation of vapor bubbles leads to normal boiling. If material heating is sufficiently rapid for the material to approach its thermodynamic critical temperature, rapid homogeneous nucleation and expansion of vapor bubbles lead to explosive boiling (phase explosion) removing solid and liquid material fragments.

When the excitation time is shorter than the thermalization time in the material, non-thermal, photochemical ablation mechanisms can occur. For instance, with ultra-
short pulses, direct ionization and the formation of a dense electron-hole plasma can lead to athermal phase transformations, direct bond-breaking and explosive disintegration of the lattice through electronic repulsion (Coulomb explosion).

In certain non-metals such as polymers and biological materials with relative long thermalization times, photochemical ablation can still occur with short-wavelength nanosecond lasers, producing well-defined ablation regions with small heat affected zones. In all cases, material removal is accompanied by a highly directed plume ejected from the irradiated zone. The dense vapor plume may contain solid and liquid clusters of material. Furthermore, the ionization of vapor during high laser intensity irradiation may lead to the generation of plasma due to the growing electron density. At this stage, the high-density plasma plume strongly absorbs the laser energy by free carrier absorption and attenuates the laser energy reaching the target. The plasma plume expansion could also lead to the generation of shockwaves. In addition, the laser-matter interactions are associated with mechanical stress due to thermal expansion or the propagation of shockwaves, which can cause another kind of ablation by spallation if the amplitude exceeds the binding strength of the lattice within the target.

7 Biomedical applications of nanoprocessing

Femtosecond NIR lasers have been employed as a medical treatment on millions of short-sighted people to optically generate the required tissue flap of several millimeters in diameter for LASIK procedures [23]. These femtosecond laser systems replace current micromechanical tools for flap generation, so-called microkeratomes. Furthermore, fs lasers are employed in ophthalmology to process the ocular lens. Relatively high pulse energies and focusing optics with a relatively low NA are employed, which enables micromachining but not nanomachining.

Medical femtosecond laser systems, such as multiphoton tomographs, have been employed for diagnostic purposes, such as early diagnosis of the skin cancer malignant melanoma [24]. The lateral resolution of these innovative high-resolution medical imaging tools is about 300 nm and the axial resolution is about 1–2 μm. Therefore, this medical imaging device is not a “real” nanotechnology device even if it is possible to image sub-100 nm single elastin fibers deep in the skin, single intratissue ZnO sunscreen particles, and tattoo nanoparticles.

The same submicron resolution applies to two-photon microscopes as the major imaging tool of cell biologists studying living cells and the brains of live transgenic mice.

Femtosecond laser nanoprocessing in living cells is feasible. Cutting and drilling with feature sizes below 100 nanometers were first demonstrated by König et al. in 1999 [25]. The group was able to nanodissect a single chromosome within a live PTK
cell without collateral effects. The cell survived and divided. The authors called this procedure nanosurgery.

Targeted transfection has become a major application of nanoprocessing of living cells, where a single foreign DNA plasmid is introduced to a cell by transient opening of the cell’s membrane, called optoporation [26]. Typically, the membrane is closed within 5 seconds due to self-repair processes.

One of the chapters of this book reports for the first time on the use of femtosecond laser transfection to introduce a cocktail of 4 plasmids into live skin cells with the purpose to realize virus-free optical reprogramming [27]. Interestingly, an extremely low mean power of some milliwatts is sufficient to realize drilling, cutting, and ablation of biological targets when using very ultrashort NIR picosecond laser pulses of 10 femtosecond pulse width and 85 MHz repetition frequency. The journal Nature Photonics termed this novel nanoprocessing technique “low-power nanosurgery” [28].

8 Technical applications

Similar to biological applications, high intensity laser pulses can be used to structure surfaces with nanometer accuracy or to use nonlinear absorption in order to induce modifications inside the bulk of a work piece. The latter is limited to materials which are transparent for the fundamental wavelength.

In surface patterning, a laser beam is scanned over a surface in a defined scheme while modifying the surface. Depending on the pulse energy, the focusing conditions and the type of material, the energy melts or ablates the material. For very high intensities, the material is sublimated directly from the solid phase. If the energy of a femtosecond laser pulse is just above the melting threshold, hydrodynamic forces can generate melt pool dynamics, which result in nanojets, i.e. very small metal peaks on the surface which exhibit quite high reproducibility. Reducing the energy by a small amount will result in polarization ripples. These kinds of regular structures have been observed in different types of materials. Their orientation is highly dependent on the orientation of the electric field vector of the incident light. Their origin is still debated by different research groups and so far, consistent models are only available for some cases. A more detailed description of the formation of low-spatial frequency and high-spatial frequency laser-induced periodic surface structures (LIPSS) will be presented in this book. A commercial application is the use of ripple formation to change the light absorption on silicon surfaces. If ripples are generated by multi-pulse exposure in SF₆ atmosphere on silicon surfaces, the reactive gas supports efficient etching. The resulting cone-like structures allow multiple reflection and absorption processes on the surfaces, increasing the total absorbance in a large spectral window. Further applications of highly oriented ripples are in microfluidic channels in order to control the fluid flow on channel or chamber surfaces. Higher laser pulse energies allow ablation of the material, directly generating holes, grooves or cuts. Another commercial appli-
cation of ultrashort laser cutting can be found in dicing of ultrathin semiconductor wafers.

Transparent media can be modified, by depositing the energy in the bulk of the material. Glass materials can be modified, for example by nonlinear absorption. Low energy femtosecond pulses, which are tightly focused below the surface, cause material changes in the vicinity of the focal point, resulting in local modifications of the refractive index. If lines are written by placing pulses next to each other, 3D waveguide structures are generated. Another often noted technique is the production of fiber Bragg gratings (FBG) in optical fibers, which are used in fiber lasers, optical telecommunication systems, and sensor applications. The standard fabrication techniques for FBG are based on the exposure to cw or long pulsed UV laser sources to induce a periodic variation of the refractive index in the fiber core. Therefore, the core is doped with germanium or hydrogen loading.

![Fig. 9: Principle of FBG generation via laser-induced volume modification of transparent materials.](image)

Another highly interesting field of investigation is the focusing of ultrashort laser pulses inside transparent polymers, inorganic crystals, and glasses, leading to local modifications of the properties of the irradiated sample without co-doping of photosensitive materials. Figure 9 shows the principle of FBG generation in fibers. Photosensitization is difficult in rare earth doped fibers, which are used in fiber lasers with FBGs as internal high reflective mirrors. The main application field here is direct writing of waveguide structures, based on a controlled change of the refractive index in laser-modified zones. The presence of ultrashort pulsed lasers has expanded the field of material processing in 3D laser micro- and nanofabrication.

To provide crack-free laser writing of permanent structures with positive refractive index changes for waveguiding applications, laser irradiation should be applied gently in an accumulative manner avoiding conditions of material failure. Several accumulation mechanisms are responsible for gentle modification of transparent ma-
terials towards waveguiding properties. At high repetition rates, the energy absorbed at the focal volume from each pulse, has no time to diffuse out before the subsequent pulse arrives, forming a point source of heat. The process of heat accumulation upon waveguide writing can be controlled by several means, including variations of pulse energy, pulse repetition rate, scanning speed, and focusing conditions.

Under intermediate irradiation conditions between the nonthermal and thermal regimes of modification of transparent materials, an intriguing phenomenon of self-assembled volume nanograting formation becomes possible. This has attracted strong interest for studies of fundamental physical mechanisms as well as for potential applications. Different research groups all over the world have demonstrated that self-organized volume nanogratings (NG) can be produced in a controlled manner, erased, and rewritten in fused silica glass. They are formed as a result of the accumulative action of several thousand linearly polarized laser pulses focused inside the material bulk and the NG layers, which are always perpendicular to the light polarization vector. It is intriguing that only three materials, fused silica, sapphire, and TeO₂, allow the inscription of the NG structures in their bulk. Nevertheless, the mechanism of NG formation is still debated and intrinsically unclear.

The generation of plasma standing waves excited by the polarized light, nanoplasm self-organization, or defect formations, are discussed as possible mechanisms. Many important applications of these amazing structures have been proposed for the development of various integrated optical and microfluidic devices and rewritable 3D optical memory storage. The grating period, usually in the range of 100 to 300 nm, decreases with laser exposure time at a fixed pulse energy, whilst increasing with pulse energy for a fixed number of applied laser pulses. NG exhibit extremely large temperature stability up to 1150 °C. The high degree of control of the structural parameters allows the fabrication of integrated highly precise phase elements, such as quarter- and half-wave plates.

In specific types of glass, a modification of the material is generated after illumination. This physical-chemical modification allows subsequent selective etching by KOH or HF. When writing a line or a certain volume, the material can then be removed by etching. Microchannels with extreme aspect ratios (up to 100) can be produced in glass or sapphire using selective laser-induced etching (SLE). Microvalves and micropumps have also been produced. The same technique has been extended to fabricate free-space optics, such as micromirrors and micro-optical lenses in glass materials.

9 Summary and outlook

UV nanosecond lasers are the major nanoprocessing tools in today’s Integrated Circuit industry. Future extreme ultraviolet technology will employ radiation at a wavelength of 13 nm. However, ultrashort laser pulses in the femtosecond range can also realize nanoprocessing, even when operating at higher wavelengths. Feature sizes one
order of magnitude smaller than the laser wavelength or less, are feasible. Furthermore, 3D nanomachining can easily be performed, such as 3D two-photon lithography and STED lithography for rapid prototyping. In-bulk nanomachining in transparent materials can be performed in contrast to standard UV nanoprocessing. Deep sub-diffraction optical two-beam lithography with 9 nm feature size and 52 nm two-line resolution has been reported based on two-photon polymerization and single-photon inhibition [29].

All-diode-based, low-cost, compact turn-key femtosecond lasers will become available within the next years. This will significantly change the market for industrial nanomachining and non-linear imaging.

References