

Chapter 1

LASER CLEANING AND SURFACE MODIFICATIONS: APPLICATIONS IN NANO- AND BIOTECHNOLOGY

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This article gives an overview of the fundamentals of laser-matter interactions with regard to the cleaning of solid surfaces from either tiny particulates or extended contamination layers. Various different applications and limitations of the technique are discussed together with surface modifications that open up completely new possibilities in nano- and biotechnology.

1. Introduction

The term laser cleaning denotes two quite different fields: the removal of *particulates* and the removal of extended *contamination layers* from solid surfaces [Luk'yanchuk 2002, Bäuerle 2000]. The latter application includes such different areas as cleaning stainless steel of scale or organic impurities, the removal of paint from metal surfaces, the cleaning of semiconductor surfaces and microelectronic or micromechanical devices, the removal of contamination layers from mechanical or electrical contacts, switches, metallic photocathodes, silicon field emitter arrays [Takai *et al.* 2002], the pretreatment of LCD-glass substrates or adhesion surface areas, etc. The application of *lasers* in the *conservation of artworks* (LACONA) has also become a rapidly growing field. Among the examples are the restoration of ancient metal artwork [Drakaki *et al.* 2004], medieval stained glass [Troll *et al.* 1999], paper [Rudolph *et al.* 2004, Kollia *et al.* 2004], paintings, frescos and stone [Zafriropulos 2002, Teule 2001, Klein *et al.* 1999] etc. With many of these applications, the removal of contamination layers can be understood in terms of laser ablation. On a wider scope, one can also include processes where a thin surface layer is “cleaned” by *outdiffusion of impurities* under the action of laser light. With systems that are

strongly inhomogeneous with respect to their optical, thermal, and elastic properties, thermo- and photomechanical mechanisms may become important. With very high fluences laser-induced shock waves and fragmentation processes are observed [Bäuerle 2000]. Clearly, these latter regimes are inadequate for well-defined cleaning of sensitive substrates and devices.

Completely *new* aspects arise with the cleaning of particulates from surfaces. Particle sizes (diameters) in the range between some 10 nm and several microns have been laser cleaned. Efficient techniques to clean off such small particulates from solid surfaces, heat-sensitive coatings, devices, etc. become increasingly important in semiconductor device fabrication, micromechanics, optics, telecommunication, etc. Here, conventional techniques such as ultrasonic and megasonic cleaning, wiping and scrubbing, high-pressure jet spraying, CO₂ snow cleaning, conventional etching, plasma cleaning etc. are often inadequate for the removal of particulate contaminations. The reason is that small particulates adhere on substrates or devices with relatively strong forces that are difficult to overcome with these traditional cleaning techniques. As a consequence, these techniques are often ineffective, result in the addition of other contaminations, the damaging of prefabricated parts, etc. It has been demonstrated that, under certain conditions and with certain systems, laser cleaning enables efficient removal of micron and submicron particles from solid surfaces.

In the present chapter, we give an overview on the applications of laser techniques to the cleaning of surfaces from both thin extended contamination layers and particulates. We start with the latter field and also discuss the submicron- and nanopatterning of surfaces by means of two-dimensional lattices of microspheres. This application can be considered as a spin-off from investigations on dry-laser cleaning of particulates from surfaces. In the fourth part we discuss the removal of contamination layers within both inert and reactive ambient media. In both cases, laser cleaning is often correlated with physical and/or chemical changes of surface properties. Among those are surface smoothing (polishing), glazing, passivation, depletion and/or substitution of particular species, the formation of stochastic or periodic structures, etc. The last part deals with laser cleaning and light-induced surface modifications of polytetrafluoroethylene (PTFE) in NH₃ atmosphere with special emphasis on applications in biotechnology.

Further details on various different topics that are only briefly discussed in this overview can be found in other chapters of this book.

2. Removal of Particulates

For cleaning-off particulates from solid surfaces, the action of the incident laser radiation must overcome the strong adhesion forces between the tiny particulates and the surface. Among these adhesion forces are mainly Van der Waals forces K_{vdw} , capillary forces K_c , and electrostatic forces K_e [Bäuerle 2000, Bowling 1995, Israelachvili 1992]. The size of these forces and their relative importance in laser cleaning depends on the size of particulates, the physical and chemical properties of particulate and substrate materials, the ambient medium etc. In fact, laser cleaning is often classified according to the ambient medium that is employed during the experiments.

Dry laser cleaning (DLC) is performed in vacuum or a dry atmosphere. If, on the other hand, the removal of particulates is assisted by the evaporation of a thin liquid film, the technique is denoted as *steam laser cleaning* (SLC). If laser cleaning is performed in an atmosphere of high relative humidity, e.g. in water vapor, we use the term *wet laser cleaning* (WLC).

In all of these different techniques, the cleaning efficiency for single-pulse laser irradiation is defined by $\eta = 1 - N_f / N_i$ where N_i and N_f are the respective surface densities of particulates before and after laser-light irradiation. η depends on the size of the adhesion forces, the laser parameters, the optical and thermal properties of both the substrate and particulate material, etc. Cleaning efficiencies achieved with N_ℓ laser pulses can be described by $\eta(N_\ell) \approx 1 - (1 - \eta)^{N_\ell}$. The number of laser pulses typically employed in laser cleaning is between 1 and 10.

Because of the various different dependences of the cleaning efficiency on the material and laser parameters, the ambient medium, the size and shape of particulates etc., investigations of fundamental interaction mechanisms require well-defined cleaning experiments with well-defined model contaminants. Well-defined contamination of the substrate surface is achieved by spin coating of colloidal solutions. Such solutions are commercially available for different materials and for particle sizes between some ten nanometers and a few microns. The size distribution of such particles is relatively narrow, typically below $\pm 10\%$. The shape of particles is often *spherical*. To avoid the coalescence of particles and the formation of aggregates during spin coating, one has to adjust the concentration of particles in the suspension, the rotation speed of the spinner, etc.

An overview on the various different systems that have been investigated can be found in [Kane *et al.* 2002].

2.1. Dry Laser Cleaning (DLC)

Dry laser cleaning can be classified into cases where particle removal relies on strong absorption of the laser light by either the substrate or the particulate, or both of them.

2.1.1. Substrate absorption

Let us first consider non-absorbing rigid (non-elastic) particulates on an absorbing semi-infinite substrate. If we ignore the influence of the particulates on the radiation field, uniform pulsed-laser irradiation will cause uniform (one-dimensional) thermal expansion of the substrate. Let us ignore also capillary and electrostatic forces between the particulates and the substrate, and set $K_c = K_e = 0$. Then, we find from Newton's law and an acceleration of particulates normal to the surface [Bäuerle 2000] the threshold fluence for cleaning

$$\phi_{cl} \approx \xi \frac{c_p}{\beta_T A} \frac{\tau_\ell^2}{r_p^q} \propto \frac{\tau_\ell^2}{r_p^q} \quad (2.1)$$

where ξ slightly depends on various different parameters. c_p is the specific heat at constant pressure, β_T the coefficient of (linear) thermal expansion, A the absorptivity, τ_ℓ the laser pulse length and r_p the radius of the particulate. q is an exponent which, for adhesion forces proportional to r_p or r_p^2 is within the range $1 \leq q \leq 2$. Within this one-dimensional (1D) model the particulates are “kicked off” from the surface due to rapid thermal expansion and subsequent contraction of the substrate. While this model is much too simple, it already shows that surface cleaning becomes increasingly difficult with decreasing particle size. An upper limit of the fluence that can be employed is set by material damage due to fracture, melting and ablation. More sophisticated 1D models take into account elastic deformations, the influence of pulse shapes, etc.

While such 1D models *qualitatively* describe some trends in laser cleaning, the calculated threshold fluence ϕ_{cl} , wavelength dependences, etc. often disagree from the experimental results by one to two orders of magnitude. This has several reasons. Among those are enhancements of the electromagnetic field underneath the particulates. These field enhancements can be related to the focusing of the incident radiation by the particle ($r_p \gg \lambda$) or to Mie-scattering ($r_p \cdot \lambda$). In any case, local field enhancements cause a *local* temperature rise in addition to the uniform temperature rise related to uniform laser-light irradiation. The local temperature rise causes local 3D-thermal expansion of the substrate material.

Calculations of this type have been performed by Luk'yanchuk *et al.* (2004), Arnold *et al.* (2004), Pleasants *et al.* (2004), and others.

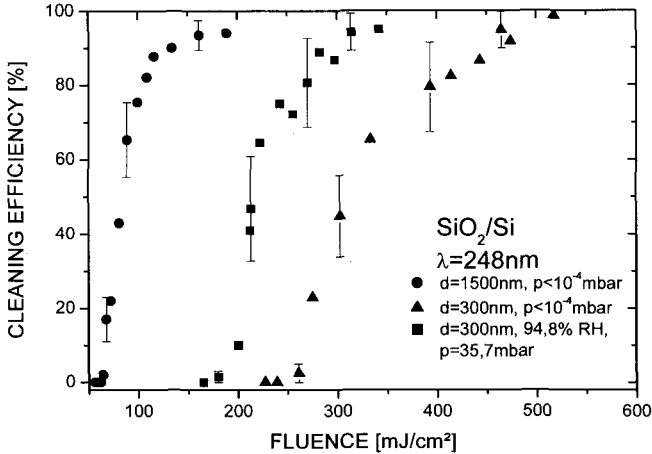


Figure 2.1: Cleaning efficiencies η achieved with single-pulse KrF-laser radiation on (100) Si substrates contaminated with spherical SiO_2 particles of diameter $d = 2r_p$. Experiments were performed in vacuum ($d = 1500$ nm, $d = 300$ nm) and water atmosphere of relative humidity $RH \approx 95\%$ ($T \approx 27^\circ\text{C}$) ($d = 300$ nm) [adapted from Schrems 2003].

Detailed *experimental* investigations have been performed on the laser cleaning of Al_2O_3 , SiO_2 , Si_3N_4 , polystyrene (PS) particulates from Si [Mosbacher *et al.* 2003, Schrems *et al.* 2003, Wu *et al.* 2000], NiP [She *et al.* 1999], glass [Pleasants and Kane 2003], and polyimide (PI) [Fourrier *et al.* 2001] substrates. Cleaning efficiencies were evaluated by either counting the particles before and after cleaning by using an optical microscope in combination with special computer software, or by measuring the change in scattered light from a HeNe probe laser illuminating the area under consideration [Chaoui *et al.* 2003]. Figure 2.1 shows the typical behavior of the cleaning efficiency of SiO_2 particles on Si as a function of fluence for KrF-laser radiation and for two different particle sizes and atmospheres. The cleaning efficiency η strongly increases above a certain threshold fluence and then remains almost constant. In *qualitative* agreement with (2.1), ϕ_{cl} increases with decreasing particle size. However, the situation may be even more complicated. With SiO_2 spheres on Si substrates strong deformation of the spheres during sample storage has been

found. Depending on the size of particulates, ϕ_{cl} can significantly increase with storage time [Schrems et al. 2003].

A detailed analysis of the threshold fluences ϕ_{cl} measured as a function of particle size cannot be explained theoretically even on the basis of 3D thermal expansion models. This is quite understandable from experimental observations. With many systems investigated so far, local substrate damage and the formation of holes underneath the particulates is observed – even with fluences $\phi < \phi_{th}$. Here, ϕ_{th} is the threshold fluence for *uniform* substrate damage/ablation. Thus, for such systems, DLC is apparently *not* based on the acceleration of particulates due to thermal expansion, but rather on local substrate ablation. Clearly, due to local field enhancement, the fluence underneath the particle, $\phi(\text{local})$, exceeds the incident uniform fluence $\phi(\text{uniform})$. This phenomenon can be used for well-defined patterning of material surfaces (see part 3).

In the present case of non-absorbing spherical particles with $r_p \gg \lambda$ the *average* intensity on the substrate surface underneath the particle can be approximated by

$$I_s \approx \begin{cases} \frac{27n^4}{(4-n^2)^3} I_0 & \text{with } \rho < \rho_c \\ 0 & \text{with } \rho > \rho_c \end{cases} \quad (2.2)$$

where n is the index of refraction of the microsphere and I_0 the (uniform) incident intensity. With $n(\text{SiO}_2) = 1.42$ we obtain $I_s \approx 14 I_0$. ρ is the distance from the axis of symmetry on the substrate surface and ρ_c the caustic radius. The latter is given by

$$\rho_c = \frac{(4-n^2)^{3/2}}{3\sqrt{3}n^2} r_p \quad (2.3)$$

With $\rho_c(\text{SiO}_2) \approx 0.27 r_p$. For transparent particles with $r_p \ll \lambda$ we can use the dipole approximation [Arnold 2003]

$$I_s = \left(1 + \frac{n^2-1}{n^2+2} k^2 r_p^2 \right)^2 I_0 \quad (2.4)$$

where $k r_p$ is the Mie parameter with $k = 2\pi/\lambda$. While the *overall* intensity enhancement by microspheres is qualitatively well described by the approximations (2.2) and (2.4), the real situation is much more complex. For

example, for transparent particles and $r_p \gg \lambda$, detailed calculations of the intensity $EE^* \equiv |E|^2$ where E is the electric field, yield a pronounced double-peak structure. This is shown in Fig. 2.2. This “fine” structure may become relevant with strongly nonlinear processes and short laser pulses. In fact, experiments using ultrashort laser pulses give clear evidence for such a distribution. Among the examples are double-hole structures observed after irradiation of PS particulates on Si substrates with 100 fs Ti:Sapphire-laser pulses [Münzer *et al.* 2002] and of SiO₂ particulates on Ni foils with 500 fs KrF-laser pulses [Bäuerle *et al.* 2003]. With longer pulses this structure is “smeared out” due to spatial dissipation of the excitation energy. Integration of $|E|^2$, $|H|^2$ or the Poynting vector $|S|$ over the caustic area $\pi \rho_c^2$ in the plane $z \approx r_p$ yields, with Mie parameters / 30, and within $\pm 20\%$, the same result as (2.2). Further details on the imaging properties of microspheres have been discussed in [Kofler 2004, Luk’yanchuk 2002]. It should be noted, however, that the scattering of the radiation reflected from the substrate yields an additional contribution to the electromagnetic field and further increases the overall intensity below the particulate [Luk’yanchuk *et al.* 2004, 2002].

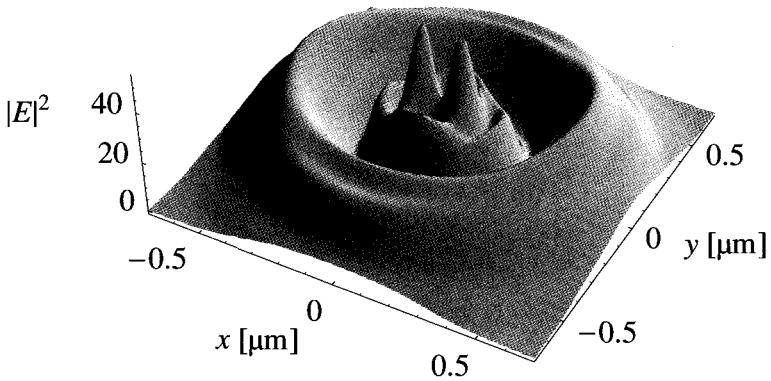


Figure 2.2: Intensity $|E|^2$ underneath a focusing microsphere at $z \approx r_p$ in the x,y -plane. The origin of the coordinate system is located in the center of a sphere with radius $r_p = 3.1 \mu\text{m}$. The incident electric field is a plane wave (wavelength $\lambda = 248 \text{ nm}$), propagating in z - and polarized in x -direction with unity strength. The refractive index of the sphere is $n = 1.42$ and the Mie parameter is $k r_p = 2 \pi r_p / \lambda \approx 78.5$. The picture was produced with the method of Bessoid matching and reveals a pronounced double-peak structure in the direction of initial polarization [after Kofler 2004].

In any case, the amplification of the intensity underneath the particulates will result in *local* ablation at fluences ϕ (uniform) $< \phi_{th}$. Threshold fluences for

“cleaning” calculated on the basis of particle removal by *local ablation* of the substrate still do not describe the experimental data quantitatively but, at least, yield more consistent slopes of the dependence $\phi_{cl} = \phi_{cl}(r_p)$ [Arnold *et al.* 2004]. A quantitative description of such a process seems to be almost impossible. Near threshold, the ablation rate and the related pressure caused by the ablated species changes drastically within a small range of fluences (local laser-induced temperature rise). Simple estimations yield pressures up to several 10^2 bar. Furthermore, with the onset of local substrate ablation, adhesion of the particulates becomes meaningless.

2.1.2. *Particulate absorption*

Experimental investigations have been performed, e.g., for SiO₂ substrates contaminated with Cu and Al particles [Lu *et al.* 1998] and for PMMA contaminated with PS particles [Fourrier *et al.* 2001]. In both cases KrF-laser radiation has been employed.

In many cases, the situation may be quite similar to that described before – except that thermal expansion of the particulate becomes important. However, with strong absorption and particulates that can be easily decomposed in a photochemical, photophysical, or thermal process, cleaning may become dominated by the *ablation* of the particles. This mechanism differs significantly from that described above. For a purely thermally activated process the fluence that causes vaporization of the particulate can be estimated from the energy balance. If we ignore thermal losses we obtain

$$\phi_{cl} \approx \frac{\rho_p}{A} \left[c_p T_v + \Delta H_v \right] r_p . \quad (2.5)$$

The physical parameters for the particulates, mainly A , make this process very selective. T_v and ΔH_v are the temperature and the enthalpy of evaporation of the particles, respectively, and ρ_p the mass density. Clearly, these quantities, and in particular the mass and the absorptivity of the particulate change during evaporation. Thus, (2.5) is only a very crude approximation.

In all cases of dry cleaning, recondensation of particulates on the cleaned substrate can be drastically reduced by employing vacuum conditions or a laminar flow of H₂ or He and an appropriate geometry of the setup with $\hat{n} \Downarrow \mathbf{g}$ or $\hat{n} \perp \mathbf{g}$ where \hat{n} is the surface normal and \mathbf{g} the acceleration due to gravity.

2.1.3. Particulate and substrate absorption

The removal of metallic particles such as Au, Cu, and W from Si [Curran *et al.* 2002] and metal surfaces has been studied by means of the fundamental and harmonics of Nd:YAG-laser radiation. Here, it has been found that substrate damage can be often diminished by using instead of perpendicular laser-light incidence glancing angles [Lee *et al.* 2000].

Surface cleaning was also demonstrated by exciting surface acoustic waves (SAW) by means of a *focused* laser beam [Kolomenskii *et al.* 1998]. In this technique, *non-local* cleaning within the region of the propagating SAW can be achieved. This region may cover an area of several millimeters around the laser-irradiated spot.

2.2. Steam Laser Cleaning (SLC)

With many systems, the removal of very small particulates from solid surfaces can be significantly enhanced by a liquid film that is deposited, e.g. via a nozzle, onto the particle-contaminated surface prior to pulsed-laser irradiation. High cleaning efficiencies have been achieved with strongly *absorbing substrates* and liquid films that are transparent at the incident laser wavelength. For example, with KrF- and Nd:YAG-laser radiation, particulates of Au, Cu, Al₂O₃, Fe₂O₃, Si, PS, etc. have been efficiently cleaned off from Si wafers and membranes [Lang *et al.* 2003; Neves *et al.* 2002, Wu *et al.* 2000; Allen *et al.* 1997; Zapka 2002]. In most experiments, the liquid film consists of water mixed with 10 to 20 % alcohol and its thickness is, typically, between about 100 nm and several μm . The alcohol improves substrate wetting.

The dependence of the cleaning efficiency on laser fluence for particles of *different* sizes (60 nm – 1300 nm) and different materials (Al₂O₃, SiO₂, PS) and geometries (spherical SiO₂ and PS and arbitrarily shaped Al₂O₃) has been investigated in [Lang *et al.* 2003, Mosbacher *et al.* 2003]. In contrast to the situation in DLC, almost the *same* cleaning threshold has been found for *all* types and sizes of particles. For other laser wavelengths and other types of substrate materials and liquid films, this threshold fluence may change significantly. In any case, the threshold fluences for cleaning required in SLC are, in general, much lower than those required for very tiny particulates in DLC. This is particularly important in connection with substrate damage or/and in situations where particles melt or/and react or form an alloy with the substrate material. Nevertheless, systematic investigations on substrate damage in SLC are still lacking.

The microscopic mechanisms that dominate SLC are not completely clear. The reason that water films are employed in most cases of SLC may be related to the high transient pressure caused by superheated water. With superheating to the critical temperature $T_{cr}(\text{H}_2\text{O}) \approx 375^\circ\text{C}$ peak pressures up to $p_{cr}(\text{H}_2\text{O}) \approx 220$ bar can be achieved. However, in a number of investigations it has been demonstrated that with the moderate laser-light intensities employed in most cases of SLC, the detachment of particulates is not related to this pressure, but to the pressure wave which results from fast-growing bubbles near and above the boiling temperature. Depending on the degree of superheating and the surface properties of the substrate, the typical pressures were measured to be . 30 bar [Kim and Lee 2003; Leiderer *et al.* 2002; Grigoropoulos and Kim 2002]. It should be noted, however, that superheating and bubble nucleation is not only determined by the laser and material parameters. Of strong influence is also the roughness of the substrate surface [Leiderer *et al.* 2002]. In any case, for micron- and submicron-sized particles, even pressures of 30 bar can cause accelerations of up to 10^{11} cm/s². Thus, although the adhesion forces for the different types of particles investigated in [Lang *et al.* 2003, Mosbacher *et al.* 2003] vary by more than an order of magnitude, the cleaning forces are so high that they exceed by far the adhesion forces for *all* of these different particulates. This may explain the “universal” cleaning threshold observed during these investigations. Clearly, the real situation may be much more complex. Cavitation effects, changes in adhesion forces, e.g. via the decrease of the Hamaker constant in water, the temperature jump at the solid-liquid interface etc. may play an important role as well.

2.2.1. *Absorbing liquid films*

Laser cleaning of polymer surfaces has been demonstrated by using KrF-laser radiation and either a strongly *absorbing* film of acetone [transmittivity $D(248\text{nm}) \approx 0$] or *transparent* isopropanol (IPA) [transmittivity $D(248\text{nm}) \approx 0.97$]. Here, efficient cleaning was achieved only with IPA and it was significantly enhanced in comparison to dry cleaning [Lee *et al.* 1998].

Steam cleaning of Si substrates from different types of particles with sizes ranging from about 0.1 to 10 μm has also been demonstrated for CO₂-laser radiation in combination with (absorbing) water films [Allen *et al.* 1997, Boughaba *et al.* 1999].

2.3. Wet Laser Cleaning (WLC)

A technique which combines some of the advantages of DLC and SLC and which avoids some of their disadvantages is wet laser cleaning. In WLC, the substrate is immersed in an atmosphere of high relative humidity (RH) of water. Thus, there is no need of any thickness control of the liquid film or synchronization of the laser pulse with the water jet. WLC avoids an overall contamination of the surface related to the liquid film. Here, the liquid condenses only in the interstices between the particulates and the substrate, where it forms a stable well-defined meniscus. For complete wetting, the volume of capillary condensed water is $V_\ell = 4 \pi R_K^2 r_p$ where $R_K \approx 0.52 / \ln^{-1}(RH^{-1})$ nm is the Kelvin radius. With $RH = 95\%$ we find $R_K = 10$ nm. Thus, the technique may be advantageous for very small particulates where the volume of the superheated water that is condensed in the interstice between the particulate and the substrate causes a high enough pressure for particle removal. Experimentally, we have found that for SiO_2 particles on Si substrates the threshold for cleaning is well below that for DLC for particle sizes $d = 2 r_p \cdot 500$ nm [Schrems 2003]. Figure 2.1 shows this influence for 300 nm particles. Further investigations in this field, in particular for particle sizes $d \cdot 100$ nm and humidities $RH > 95\%$, seem to be quite promising. A larger water meniscus would certainly favor bubble formation.

3. Submicron- and Nanopatterning

The local field enhancement observed below and near particulates in dry laser cleaning may result in local material ablation and/or in physical and chemical surface modifications. This phenomenon can be employed for single-step surface patterning. Besides of stochastic patterns, well-defined periodic structures can be fabricated. In the latter case we employ regular two-dimensional (2D) lattices of microspheres which form by well-known self-assembly processes from the colloidal suspensions already mentioned before. Because of their thermal stability and optical properties, we mainly employ microspheres of a- SiO_2 and a transparent support. The microspheres act like microlenses and focus the incident laser radiation onto the substrate, albeit with significant (spherical) aberration. Due to aberration the maximum intensity is shifted from the geometrical focus

$$f = \frac{n}{n-1} \frac{r_p}{2} \quad (3.1)$$

to the diffraction focus

$$f_d \approx f \left(1 - \sqrt{\frac{3\pi}{4kr_p} \frac{n(3-n)-1}{n(n-1)}} \right). \quad (3.2)$$

This expression approximates the position of the maximum intensity within an error of $< 5\%$ for $kr_p / 100$ and values of the refractive index $1.4 < n < 1.6$. Besides of primary patterns, subpatterns (secondary structures) have been observed for substrate distances that exceed the focal length of the microspheres. These secondary structures originate from interferences of beams propagating from single microspheres.

The 2D lattices of microlenses permit one to produce on a substrate surface thousands or millions of single submicron features with a single or a few laser shots. By using single-shot-laser radiation and a fused quartz support with a monolayer of a-SiO₂ spheres of various diameters, we have demonstrated various different types of surface patterning. Among the examples are 2D ablation patterns on polymers [Denk *et al.* 2002; Piglmayer *et al.* 2002], arrays of circular cones on (100) Si wafers [Wysocki *et al.* 2003], and holes in W films that have been etched in WF₆ atmosphere. Arrays of W and Pd dots have been deposited from gaseous mixtures of WF₆ and H₂ [Denk *et al.* 2003] and from aqueous solutions of PdCl₂ in NH₃ [Bäuerle *et al.* 2004, 2003], respectively.

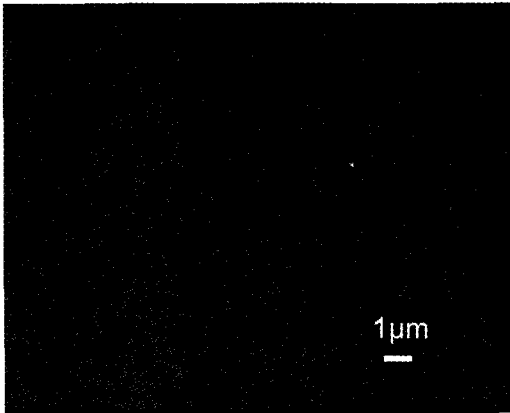


Figure 3.1: YBa₂Cu₃O_{7.8} film on (100) MgO patterned by means of 248 nm KrF laser radiation ($\tau_p \approx 24$ ns) and a 2D lattice of a-SiO₂ microspheres ($d = 1.5 \mu\text{m}$) [after Brodoceanu *et al.* 2005].

Figure 3.1 shows a typical hexagonal pattern generated by means of a 2D lattice of microlenses and a single KrF-laser pulse on a thin film of YBa₂Cu₃O_{7.8}

on a MgO substrate. In such a primary pattern, the distance between neighboring spots is equal to the size of the microspheres, $d = 2r_p$. It has already been demonstrated in [Liberts *et al.* 1988] that laser-light irradiation of high-temperature superconductors causes a depletion of oxygen and thereby changes the material properties from superconducting to semiconducting ($\delta / 0.45$). The dark dots in Fig. 3.1 consist of small humps with a maximum height of 5 to 8 nm with, probably, local depletion of oxygen. Such a structure may yield additional well-defined periodic pinning centers for vortex “lines” [Brodoceanu *et al.* 2005].

Well-defined surface “roughening” based on secondary intensity maxima has been demonstrated for polyethylenephthalate (PEN). The dimensions of the structures are significantly smaller than those of the corresponding primary structures [Bäuerle *et al.* 2003].

Laser-induced forward transfer (LIFT) has been performed by using thin metal foils in close contact between the microspheres and the substrate. By this means, hexagonal patterns of metal dots on arbitrary substrate materials together with the corresponding holes in the metal foils have been produced by single-shot KrF-laser irradiation. Similar patterns have been generated from metal films that were directly evaporated onto the surface of the microspheres. Scanning electron microscope (SEM) pictures of the 2D lattice of microspheres *after* the LIFT process reveal that the evaporated film is removed from the surfaces of spheres only within a certain region of diameter ρ . Similar to the size of the metal dots generated on a substrate, ρ depends on the size and index of refraction of the microspheres, the type and thickness of the evaporated film, and the laser parameters [Landström *et al.* 2004, Bäuerle *et al.* 2003]. In any case, this technique permits one to generate a 2D lattice of microlenses with well-defined apertures. Such a system can be employed, e.g., as a highly efficient contact mask. Due to the focusing nature of the microspheres, the incident intensity can be almost totally used for surface patterning. The situation is quite different to standard shadow masks where a significant amount of the incident intensity is lost. The amplification of the local intensity related to the focusing microspheres is of the order of $(r_p/\lambda)^q$ with $1 < q < 2$. Thus, with the present conditions we obtain an amplification factor of 10 to 100 in comparison to a shadow mask.

Figure 3.2 shows a 2D lattice of microspheres with apertures $\rho < \rho_c \approx 0.53 \mu\text{m}$. Apertures with $\rho < \lambda$ are particularly well suited for investigating near field effects.

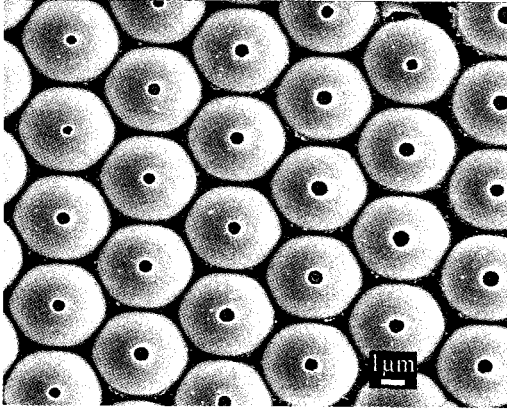


Figure 3.2: Apertures fabricated on a 2D lattice of SiO_2 microspheres ($d = 4 \mu\text{m}$) covered with 75 nm Au by single-pulse Ti:Sapphire-laser irradiation ($\lambda \approx 800 \text{ nm}$, $\tau_p \approx 120 \text{ fs}$) [after Langer *et al.* 2005].

4. Removal of Contamination Layers

The removal of contamination layers from technical or medical devices or from art work is mainly based on pulsed-laser ablation (PLA). Pulsed-laser ablation permits one to widely suppress the dissipation of the excitation energy beyond the volume that is ablated during the pulse. This is fulfilled if the thickness of the layer ablated per pulse, Δh , is of the order of the heat penetration depth, $l_T \approx 2(D\tau_c)^{1/2}$ or the optical penetration depth $l_\alpha = \alpha^{-1}$, depending on which is larger

$$\Delta h \approx \max(l_T, l_\alpha) \quad (4.1)$$

Here, D is the heat diffusivity and α the absorption coefficient. This (simplified) condition is, in fact, the basic requirement for applications of the technique in laser cleaning. With fluences around and above the threshold fluence for ablation, i.e. with ϕ / ϕ_{th} we can employ the approximation $\Delta h \propto \phi - \phi_{th}$. This relation holds for thermal, photophysical, and photochemical ablation mechanisms which have been discussed in detail in [Bäuerle 2000].

With laser radiation that is strongly absorbed within the contamination layer, pulsed-laser ablation permits one to remove such layers with a single or multiple pulses and submicrometer thickness control. This is a very important property of the technique and a prerequisite for many applications such as the cleaning of prefabricated devices, the restoration of paintings etc. Furthermore, contrary to mechanical tools or chemical techniques, laser light avoids any contamination of the material being processed. With many systems, the threshold

fluence for substrate ablation exceeds the fluence required for the removal of the contamination layer. In such cases, cleaning becomes self-terminated. This process can be optimized via the laser parameters, in particular the laser wavelength and pulse duration. With medical and biological applications it is also important that laser beams are absolutely sterile tools.

With strongly inhomogeneous systems where the physical (optical, thermal, elastic, etc.) properties of the contamination layer differ significantly from those at the underlying material, thermo- and photomechanical ablation mechanisms may become important [Bäuerle 2000]. Stresses (pressures) related to such mechanisms can cause crack formation, exfoliation (removal of macroscopic fragments or flakes), instabilities etc. Thus, cleaning becomes uncontrolled and may cause substrate damage. With sensitive substrate materials and devices, it is important to suppress such mechanisms by choosing adequate laser parameters. Here, it is often sufficient to use short enough laser pulses and a wavelength that is strongly absorbed by the contamination layer.

With very high fluences, laser-induced shock waves become increasingly important in material ablation and fragmentation processes. Clearly, this regime is inadequate for the cleaning of sensitive substrates and devices.

With many systems, the removal of a contamination layer causes also physical and/or chemical modifications of the surface. Such surface modifications may be advantageous or disadvantageous, depending on the particular system and application. Finally, a reactive ambient medium may significantly enhance laser cleaning rates and cause well-defined surface modifications.

4.1. *Surface polishing and glazing*

With some applications it is essential that the removal of the contamination layer is correlated with a polishing (smoothing) or glazing of the surface. The mechanisms of these processes have been discussed in [Bäuerle 2000]. Clearly, surface smoothing decreases the effective surface area and thereby suppresses rapid recontamination based on physical, chemical or biological processes. Additionally, surface smoothing may decrease tribological effects, increase the optical transparency of the material, etc. A recent example for the latter application is the ablation and polishing of polytetrafluoroethylene (PTFE) foils for various different applications, as e.g. for liquid crystal displays (LCD). Figure 4.1 shows scanning electron microscope (SEM) pictures of a rough PTFE foil before and after F_2 -laser irradiation in N_2 atmosphere. The untreated surface shows a fibrous structure which is typical for this type of dense PTFE. The

average surface roughness measured by means of an atomic force microscope (AFM) is $R_A = 127$ nm. The aspect ratio of this roughness defined by the steepest slope found on any typical traverse scan by the AFM-cantilever was at least $20\bar{E}$. This value is determined by the resolution of the AFM cantilever which cannot recess in between the fibers. Thus, the real aspect ratio is much higher.

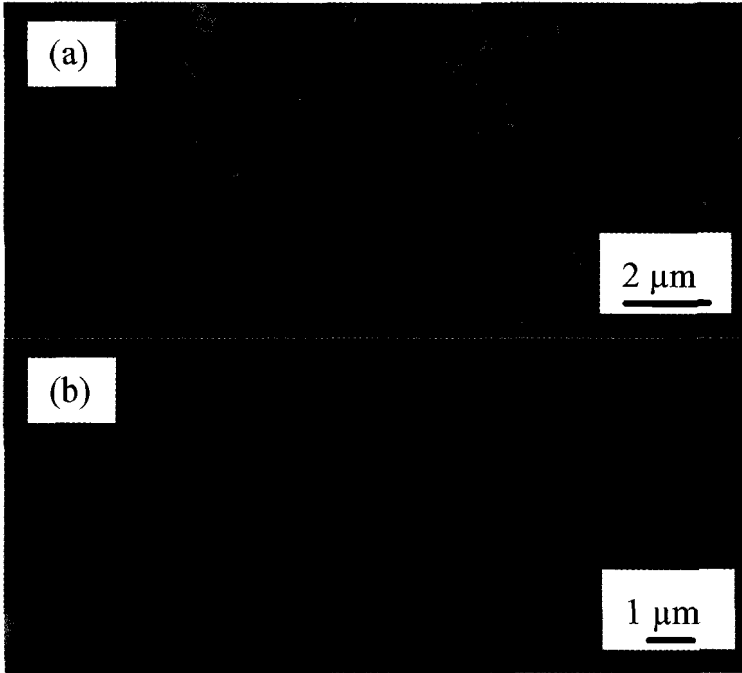


Figure 4.1: SEM pictures of a 40 μm thick PTFE foil. (a) Original surface showing fibrous structure of dense PTFE. (b) After irradiation with 157 nm F_2 -laser light ($\phi = 20$ mJ/cm^2 , pulse repetition rate $\nu_r = 20$ Hz, number of pulses $N_t = 1003$) in N_2 atmosphere at $p(\text{N}_2) \approx 1.1$ bar [after Gumpenberger *et al.* 2005b].

Figure 4.1b shows the same foil after 157 nm F_2 -laser irradiation in N_2 atmosphere. The laser-treated surface is smooth and featureless. The surface roughness is $R_A \approx 64$ nm and the aspect ratio about $3\bar{E}$. While the total optical transmission of treated and untreated foils is almost the same within the wavelength region $250 \text{ nm} \leq \lambda \leq 800 \text{ nm}$, the collimated transmission – in particular within the region between 250 nm and 600 nm – is significantly increased in laser-treated samples. The decrease in light scattering observed in

such polished samples can also be seen from the reflectivity spectra in Fig. 4.2. The laser-induced temperature rise can be estimated from Eq. (7.5.2) in [Bäuerle 2000]. For a fluence of $\phi \approx 5 \text{ mJ/cm}^2$ and a pulse length of about 20 ns we obtain $\Delta T \approx 350^\circ\text{C}$. This temperature rise agrees quite well with the decomposition temperature of PTFE. Clearly, this estimation does not account for the influence of the surface roughness and the related dimensionality of heat diffusion.

Surface smoothening together with glazing is an important “side effect” in some cases of laser cleaning of stone reliefs, sculptures, and buildings. Glazing increases the surface hardness and decreases its porosity.

4.2. *The influence of an ambient medium*

A *non-reactive* ambient medium may influence the cleaning process in various different ways. Among those are the transport of the material removed from the surface, the attenuation of the incident laser light, and the promotion of surface instabilities. For gaseous media, all of these effects become more pronounced with increasing pressure.

In many cases it is advantageous to clean off contamination layers by irradiating the surface in the presence of a *reactive* ambient medium. Such a medium may enhance the cleaning efficiency and/or suppress physical or chemical changes of the surface and/or passivate or modify the surface simultaneously with cleaning. The enhancement of ablation or etch rates in gaseous and liquid ambient media has been discussed in detail for various different systems in [Bäuerle 2000].

5. Surface Modifications of PTFE, Applications in Biotechnology

Fluorocarbon polymers are widely used in various different fields of physical and chemical technology, in medicine and biotechnology. The wide range of applications of these materials is related to their high chemical resistivity and thermal stability, to their low adhesion properties, their low electrical conductivity and wettability for various liquids, etc. For applications that require a coating or hydrophilic/lipophilic properties of the surface, either the whole surface or restricted areas thereon must be modified. To achieve this, radiation treatment has been extensively investigated [Gumpenberger *et al.* 2005a, Benson 2002, Bäuerle 2000]. In this paragraph we discuss our present activities in this field, in particular with respect to applications in biotechnology.

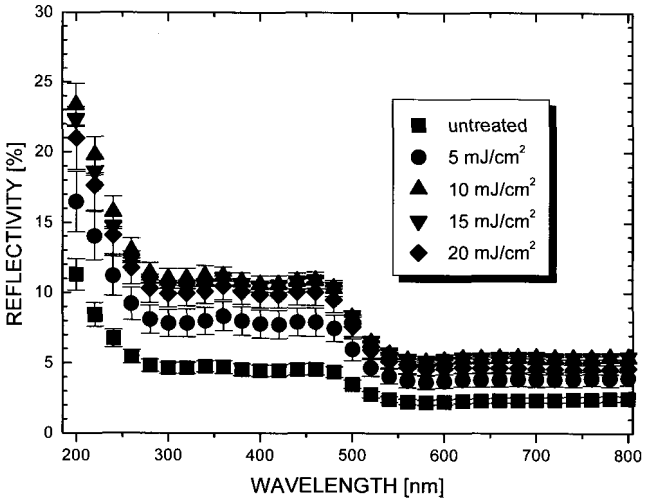


Figure 4.2: Reflectivity spectra of PTFE foil (40 μm) treated with 157 nm F_2 -laser radiation at different fluences in N_2 atmosphere (pulse repetition rate $\nu_r = 20$ Hz, scanning velocity of the irradiated area on the sample surface $\nu_s = 40$ $\mu\text{m}/\text{s}$, $p(\text{N}_2) \approx 1.1$ bar). Measurements were performed with an Au mirror as reference [after Gumpenberger *et al.* 2005b].

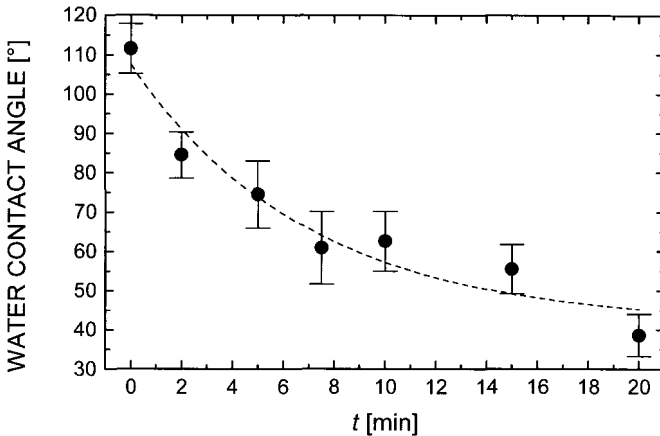


Figure 5.1: Water contact angle on dense PTFE versus time of irradiation with 172 nm Xe_2^* -light in 5 mbar NH_3 [Gumpenberger *et al.* 2005b].

Figure 5.1 shows the water contact angle of PTFE surfaces for 172 nm Xe_2^* -lamp irradiation in NH_3 atmosphere. The biocompatibility of surfaces treated in this way was evaluated by seeding biological cells onto them. Figure

5.2 shows the population density of human umbilical vein endothelial cells (HUVEC) on untreated and treated PTFE for both different irradiation times and times of cultivation. For comparison, results achieved with standard polystyrene (PS) Petri dishes have been included as a reference. First of all, good adhesion of cells is observed only on irradiated PTFE surfaces. Here, the cells start to proliferate and then grow to dense confluent multiple layers within about 8 days. The population densities are comparable to those achieved in PS Petri dishes. On untreated PTFE, the number of cells does not change significantly even after 8 days. For *all* samples, the population density of cells immediately after seeding is much lower than the density of seeded cells ($76\,000\text{ cells/cm}^2$; full line in Fig. 5.2).

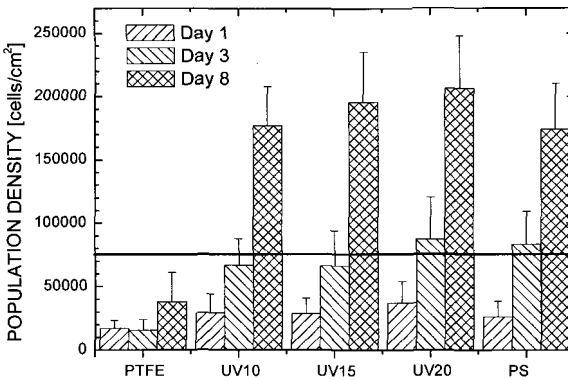


Figure 5.2: Population densities of human umbilical vein endothelial cells (HUVECs) on various samples after 1, 3 and 8 days of cultivation. PTFE: untreated material; UV10: PTFE surface exposed to 172 nm Xe₂⁺-light in 5 mbar NH₃ for 10 min; UV15: 15 min; UV20: 20 min; PS: standard polystyrene Petri dish [adapted from Gumpenberger *et al.* 2003].

The high wettability and biocompatibility of treated surfaces is ascribed to polar groups introduced into the PTFE surface by substitution of F atoms. The subtraction of F is mediated via atomic H which is generated in the dissociation reaction $\text{NH}_3 + h\nu (172\text{ nm}, 193\text{ nm}) \rightarrow \text{NH}_2 + \text{H}$. Here, 172 nm radiation is more efficient with respect to the wettability achieved, but it also causes more structural damage of the material surface than 193 nm ArF-laser radiation. The high wettability is correlated with an enhanced biocompatibility of the surface. This is either due to the adsorption of adhesion-mediating proteins from the cell culture medium or due to direct interactions of the cell membrane, or specific

receptors thereon, with the new species that substitute F in the modified PTFE surface.

Endothelial cells as, e.g., HUVECs, form the inner surface of blood vessels in direct contact with the blood stream. They play an important role in the avoidance of thrombosis, the immuno-response after injuries or the vascularization of tissues [Alberts *et al.* 2002]. Therefore, they are regarded as the optimal coating for artificial blood vessels, which are currently fabricated either from expanded PTFE or from knitted polyethyleneterephthalate (PET) fibers. The biocompatibility of both polymers can be improved by UV-irradiation in a reactive atmosphere [Heitz *et al.* 2004]. This offers the possibility to coat artificial blood vessels before implantation with the own (autologous) endothelial cells of the patient.

Modified PTFE surfaces show a high degree of biocompatibility with good cell adhesion and proliferation, which is confined to the irradiated areas. However, the UV-treatment results also in a loss of mechanical stability due to the scission of polymer chains, especially for light-sources with wavelengths below 193 nm [Gumpenberger *et al.* 2005a]. Figure 5.3a shows the decrease in tear strength of thin PTFE foils with increasing time of 172 nm Xe₂*-lamp irradiation. This decrease in mechanical stability can be diminished by creating only “pinning centers” for cell adhesion instead of uniform modification of the surface. Cell adhesion to extra-cellular proteins as, e.g., collagen, fibronectin, or fibrin, is based on interactions of receptors in the cell membrane with specific ligands in the proteins. The adhesion receptors with dimensions of, typically, 10 nm, are not homogeneously spread in the cell membrane, but form local adhesion points with lateral dimension of about 1 μm [Alberts *et al.* 2002]. Therefore, by diminishing photochemical surface modifications to spots with a diameter of about 1 μm and with a suitable spacing, cell adhesion similar to that obtained with homogeneously modified surfaces should be achieved. In preliminary experiments, we have demonstrated this by using again a 2D lattice of SiO₂ microspheres ($d = 6.8 \mu\text{m}$). The result is shown in Fig. 5.3b. The PTFE sample was first irradiated for 30 min through the 2D lattice of microspheres with 172 nm Xe₂*-light in 5 mbar NH₃. Subsequently, the microspheres were removed and HUVECs were seeded onto the surface after sterilization. Adhesion and proliferation of the HUVECs on such locally modified surfaces was similar to that on homogeneously irradiated surfaces. Again, cells did not adhere on non-irradiated areas. The distance between the dark points in Fig. 5.3b is equal to the diameter of the SiO₂ microspheres. We assume that these points are

formed by local photochemical modification of the PTFE surface due to focussing of the light by the microspheres.

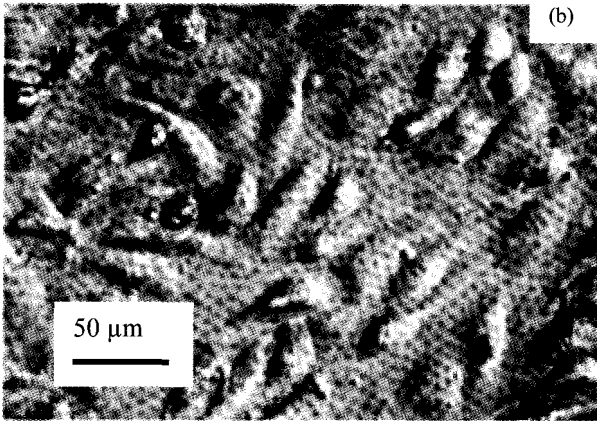
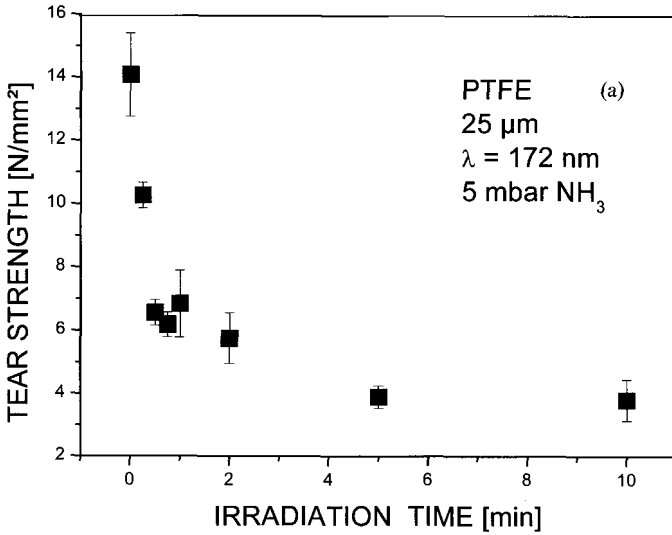


Figure 5.3: Modification of PTFE foil by 172 nm Xe_2^* light in 5 mbar NH_3 . a) Change in tear strength with irradiation time [adapted from Gumpenberger *et al.* 2005b]. b) Phase contrast microscope picture of HUVECs grown on a PTFE surface irradiated for 30 min through a 2D lattice of SiO_2 microspheres ($d = 6.8 \mu\text{m}$). The image was taken 4 days after seeding with 64 000 cells/ cm^2 [after Bäuerle *et al.* 2005].

The selectivity of adhesion and growth of cells can be tested by irradiating the surface with 172 nm Xe₂⁺-light through a contact mask. Phase contrast microscope pictures of such surfaces taken 3 days after seeding with HUVECs and for different seeding densities are shown in Figs. 5.4a,b. If we define the selectivity of adhesion by the ratio of the number density of cells on the irradiated spots and the total number density of cells $N^* = N_{\text{spots}} / N_{\text{total}}$, we find that N^* is between 70 % and 90 %. This is a very high value, in particular if we take into account that only about 8.7 % of the total surface was irradiated. The high selectivity and resolution achieved in these experiments are very promising with respect to applications of this technique in the fabrication of micro-cell arrays. Such micro-cell arrays permit high-throughput analysis of gene functions, pharmacological testings, etc. in living cells [Ziauddin and Sabatini 2001, Wu *et al.* 2002, Silva *et al.* 2004]. Miniaturization also allows efficient use of potentially rare cells or biological samples. Furthermore, such cell arrays are very useful for cell multiplexing, because hundreds of arrays can be produced from a single set of source plates.

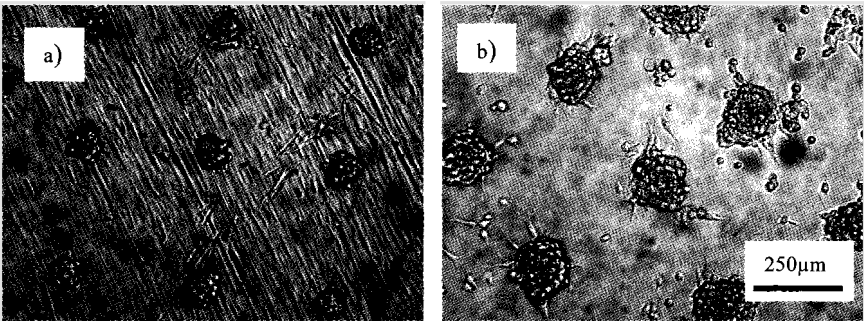


Figure 5.4: Phase contrast microscope pictures of HUVECs grown on a PTFE surface irradiated through a contact mask for 20 min with 172 nm Xe₂⁺-light in 5 mbar NH₃. The images were taken 3 days after seeding with (a) 21 000 cells/cm² (b) 32 000 cells/cm² [adapted from Mikulikova *et al.* 2005].

Cell arrays, maybe even single-cell arrays with one cell per spot can also be fabricated by generating pinning centers by means of the microsphere technique. Clearly, the spacing between such centers must exceed at least the dimensions of single cells. Such a technique would have a wide range of novel applications.

6. Conclusions

Investigations on laser cleaning of solid surfaces from submicron- and nano-particulates have led to a deeper understanding of fundamental laser-matter interaction processes. Local substrate damage observed in many cases of dry laser cleaning (DLC) is unacceptable for most applications under consideration. Among the exceptions may be systems where, e.g., strongly absorbing “dust” particles can be easily evaporated/ablated without substrate damage. The situation is more promising with steam laser cleaning (SLC). The “universal threshold” observed in the experiments permits one to clean with essentially the same laser fluence substrates that are contaminated with particulates of different sizes and shapes and which consist of different materials. For submicron- and nano-particulates the threshold fluences are much lower than those required in DLC. However, whether SLC really becomes an adequate tool for large-scale applications is not yet clear. Here, further investigations with respect to possible surface modifications, the optimization of process parameters and efficiencies, the improvement of the reliability of the technique, etc. are certainly required. Wet laser cleaning (WLC) may combine advantages of DLC and SLC. At present, however, the few investigations performed in this area do not permit any conclusions. Local field enhancements observed in the vicinity of particulates in DLC can be employed for various different kinds of surface patterning. The technique permits one to generate both stochastic and periodic structures with variable surface densities and feature sizes below 100 nm in a single processing step.

Laser cleaning of solid surfaces from extended contamination layers is a well-established field. Cleaning can be performed in an inert or in a reactive ambient medium. Applications range from the cleaning of small devices up to extended areas including different types of artwork and even whole buildings. The removal of contamination layers often causes physical and/or chemical modifications of the surface. Among those are surface smoothing, densification and glazing, changes of the optical and wetting properties of the surface, etc. Laser cleaning together with such changes in surface properties open up completely new applications in various different fields of device- and biotechnology.

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