Lithography

1 Survey

Greek λιθοσ 'a stone' and γραφειν 'to write', the art of printing from stone is one of the most important of the graphic arts ...[1]

This short explanation found in an encyclopaedia is followed by several pages describing the different methods of this art. This explanation is right, but does not cover the meaning which is the topic of this chapter. Here *lithography* addresses the key technology of semiconductor fabrication, the definition of lateral structures.

One of the fundamentals of our society is the storage and handling of information. The need for quicker processing of more and more data is the driving force for the development of microelectronic devices. In 2000 the critical dimensions of most important microelectronic devices, the Metal Oxide Semiconductor Field Effect Transistors (MOSFET), which are the heart of almost every integrated circuit, are about 180 nm; in 2001 this measure will be scaled down to 130 nm. The International Technology Roadmap for Semiconductors [2], which identifies the technological challenges and needs facing the semiconductor industry over the next 15 years, indicates a further shrinkage of this dimension down to 45 nm in the year 2013. This rapid development requires a huge amount of research and the advancement of new technologies.

A brief insight will be given here into the ongoing methods of lithography and the physical limitations. In Sec. 1 a survey is given, in Sec. 2 so-called optical lithography and its progress are discussed in detail. In Sec. 3 extreme ultra violet lithography and in Sec. 4 x-ray lithography are discussed. Another promising candidate for sub-100 nm patterning is lithography with electrons, which is described in Sec. 5, while lithography with ions is addressed in Sec. 6. Sec. 7 deals with the matter of resists and in Sec. 8 an insight in the issue of the alignment of several mask layers is given. As an example of non-lithographic patterning, "nano-imprint Lithography" is introduced in Sec. 9.

The term "lithography" describes the method with which a pattern is defined on a sample. A lithographic system consists of a radiation source, a resist-coated sample and an image control system that regulates which part of the sample is illuminated by the radiation and which is not (Figure 1a). The resist is changed by the illumination (Figure 1b). Depending on the type of resist, the exposed (positive tone process) or the unexposed resist (negative tone process) can be removed selectively by a developing process (Figure 1c). The pattern is now inscribed into the resist and can be transferred to the sample by a subsequent process step, e.g. an etching step. The name *resist* stems from this step, which is not actually part of the lithography process: The resist is resistant to the etching agent, so that the parts of the sample which are still covered by the resist are protected against etching.

Figure 2 shows a survey of the different types of lithography. They differ according to the type of radiation and the control system. However, the starting point of the process is the structure, which has to be transferred to the sample; it is normally given as a

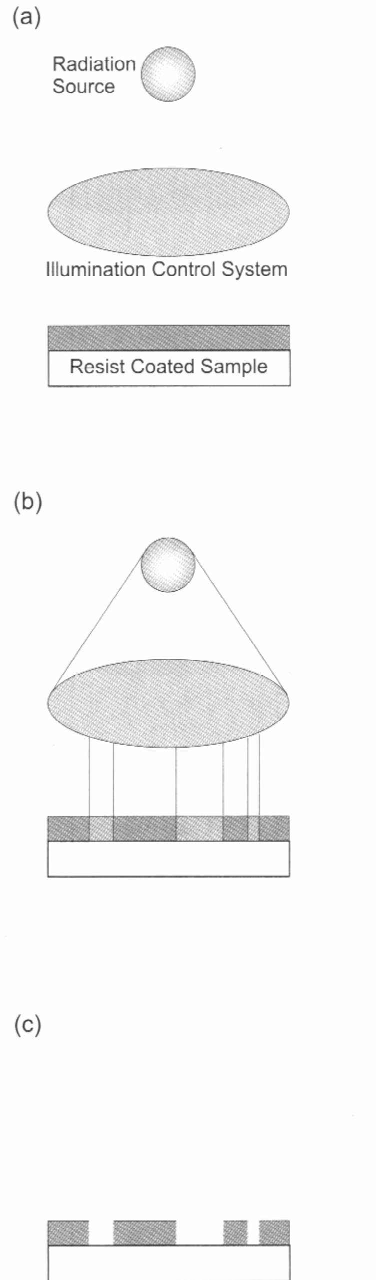


Figure 1: Schematic process flow of lithography with a positive tone resist: (a) A lithographic system consists of a radiation source, an illumination control system and a resist-coated sample; (b) Illumination Process: The resist is changed by the radiation, (c) Development: The illuminated resist can be etched selectively to the unexposed resist.

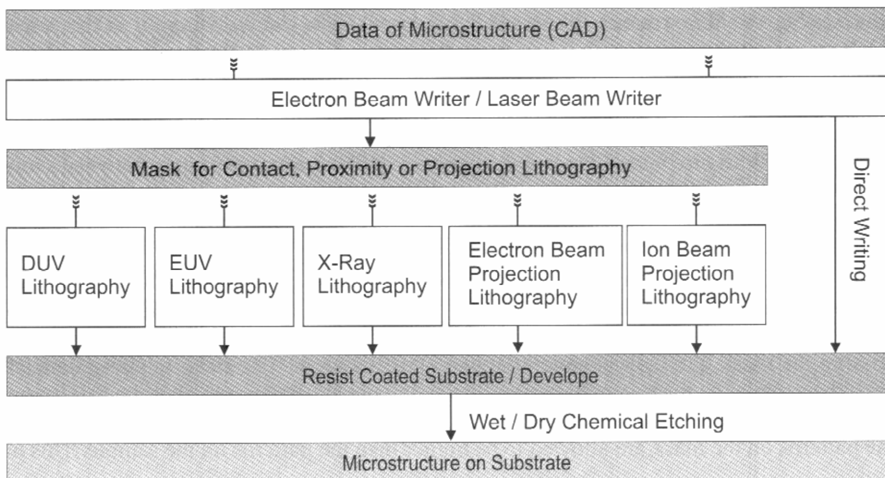


Figure 2: Survey of the different types of lithography.

CAD-file. The use of light as radiation yields so-called *optical lithography*. Depending on the wavelength, a distinction is made between ultraviolet (UV: 365 nm – 436 nm), deep UV (DUV: 157 nm – 250 nm), extreme UV (EUV: 11 nm – 14 nm) and x-ray (< 10 nm). The use of electrons or ions as radiation yields electron or ion lithography, respectively.

As the image control system either a *mask* is used, which yields *contact, proximity* or *projection lithography*, or the patterns are directly written into the resist by a focused beam (*laser, electron* or *ion beam lithography*).

With the first method, the mask consists of a carrier material, which is transparent for the radiation used, and an absorber layer, which is opaque. Into this opaque layer, the pattern is inscribed. The material depends on the radiation source and is addressed later. The radiation will only illuminate those parts of the sample where the corresponding part of the mask is transparent. Therefore only at those parts the resist is exposed and hence changed.

With *direct writing* a computer controls a focused beam of the used radiation. With deflecting units, the beam is scanned across the sample so that the pattern is written into the resist as if using a pen. Here every pattern has to be written after the other so that it takes a long time to finish a whole wafer. The development process is the same as for mask-based lithography. The relevancy of direct writing lies in its research purpose and in mask fabrication. There the mask itself is the resist-coated sample.

2 Optical Lithography

Optical lithography is the most important type of lithography. Originally the name referred to lithography using light with wavelength in the visible range. Nevertheless, gradually, the wavelength was driven down to 193 nm, which is used in semiconductor production nowadays, and even shorter wavelengths down to the sub-nm rage are under investigation.

The key issue of lithography is the resolution of the system, and hence the size of the smallest feature (minimum feature size: *MFS*) which can be defined on the sample. This *MFS* depends on the illumination method, the illumination wavelength λ, on the materials of the optical system and the resist used. In Sec. 2.1 the different illumination methods and their physical resolution limits are addressed, in Sec. 2.2 the wavelengths and the light sources are discussed, also for wavelengths below 15 nm, while lithography with these wavelengths is discussed in Sec. 3 and 4, and in Sec. 2.3 the materials and the forms of the optical system are dealt with.

2.1 Illumination Methods and Resolution Limits

Figure 3 shows a schematic view of the three different illumination methods *contact, proximity* and *projection lithography*. With all three, the light emitted by a light source passes a condenser optics so that a parallel beam is formed. With contact lithography, mask and sample are pressed together so that the mask is in close contact to the resist (Figure 3a). The resolution is limited by deflection and is expressed by the *MFS* which can be obtained. For contact lithography this is: $MFS = \sqrt{d \cdot \lambda}$, where d is the resist thickness and λ the wavelength. For a resist thickness of 1 µm and a wavelength of about 400 nm, this yields a minimum feature size of 600 nm. The major drawback of this method is that the quality of the mask suffers from contact to the resist, leading to failures in the structure. To avoid this problem, the second method was developed (Figure 3b). With *proximity lithography* there is a defined proximity gap g between sample and mask, so there is no deterioration of the mask. The drawback is the poorer resolution limit, which is proportional to $\sqrt{(d+g) \cdot \lambda}$. With same figures as above and a proximity gap of 10 µm, the *MFS* is 2 µm.

The method used today in industrial production is so-called *projection lithography* (Figure 3c). Here not the shadow of the mask is transferred to the sample as with the two other methods, but a picture of the mask is projected onto the sample. Therefore after passing the mask, the light is bundled by an optical system. The mask is not in contact with the sample, so there is no deterioration as in contact lithography, but the resolution is better than in proximity lithography. Furthermore it is possible to reduce the picture so the patterns on the mask are allowed to be bigger than the patterns on the sample. This is

advantageous for mask fabrication: Errors are also reduced. If it is possible to obtain masks with an accuracy of 100 nm, then the error for a structure of 500 nm to be transferred onto a sample is 20 %, if it is transferred one by one. If the picture is reduced 4 times, then for a 500 nm feature on the sample, the feature on the mask has to be 2 µm; therefore the mask error is only 5 %. Because of the reduction, the wafer is not exposed in one exposure, but in several . This is done by so-called steppers, in which the wafer is adjusted under the mask by an x-y-table. The stepper moves the wafer from one exposure position to the next, while the mask is not moved.

In projection lithography the limiting factor to the MFS is diffraction. Consider a slit width b which is illuminated by a monochromatic plane wave. What will the intensity distribution look like on a screen at a distance l behind the slit? Therefore consider two Huygens waves, one from the lower rim of the slit, one from the middle. There will be an optical path difference between these two Huygens waves, depending on the angle of propagation Θ. The magnitude of the path difference (PD) is:

$$PD = \frac{b}{2}\sin(\Theta) \tag{1}$$

The two Huygens waves will interfere destructively if the PD is an odd multiple of the half wavelength:

$$\frac{b}{2}\sin(\Theta_{\min}) = (2m+1)\cdot\frac{\lambda}{2} \qquad \text{with } m = 0, \pm 1, \pm 2, \ldots \tag{2}$$

Under this condition, the Huygens waves from the lower part of the slit will interfere destructively with the ones from the upper part. At the angle Θ_{min} there is a minimum of intensity.

The Huygens waves do interfere constructively resulting in a maximum of intensity when:

$$\frac{b}{2}\sin(\Theta_{\max}) = m\lambda \qquad \text{with } m = 0, \pm 1, \pm 2, \ldots \text{ holds.} \tag{3}$$

In lithography the diffraction patterns of several structures are superimposed so the question leading to the MFS is the question of when two structures can be resolved. The first approach is given by the Rayleigh criterion [3]. When light coming from a point source passes an optical system a blurred diffraction pattern – the Airy disc – occurs. The Rayleigh criterion says that two ideal point sources (e.g. stars) can be resolved when the intensity maximum of the one Airy disc is in the first minimum of the other, so MFS is given as:

$$MFS = 0.61\cdot\frac{\lambda}{NA} \tag{4}$$

where NA is the numerical aperture of the optical system. Nevertheless the Rayleigh criterion is just a first approach to the MFS in microlithography. The mask patterns are not independent (i.e. incoherent) ideal point sources, on the contrary they have a finite width and the light is partially coherent. Nevertheless, the form of the criterion gives the right dependences. If the wavelength is decreased by 10 % or the NA is increased by 10 %, the MFS is improved by 10 %. Furthermore, it was derived only by properties of the optics although the photoresist also affects the MFS. Therefore more generally, the criterion is written as:

$$MFS = k_1\cdot\frac{\lambda}{NA} \tag{5}$$

where k_1 is a constant (typically 0.5 – 0.9), which accounts for non-ideal behaviour of the equipment (e.g. lens errors) and the influences which do not come from the optics (resist, resist processing, shape of the imaged structures,...). Therefore k_1 is called the technology constant.

As a comparison, for a technology constant of 0.7 and a numerical aperture of 0.7, which are commonly used figures, the MFS is in the order of the wavelength λ. So it is better by about a factor of 0.66 than the MFS of contact printing.

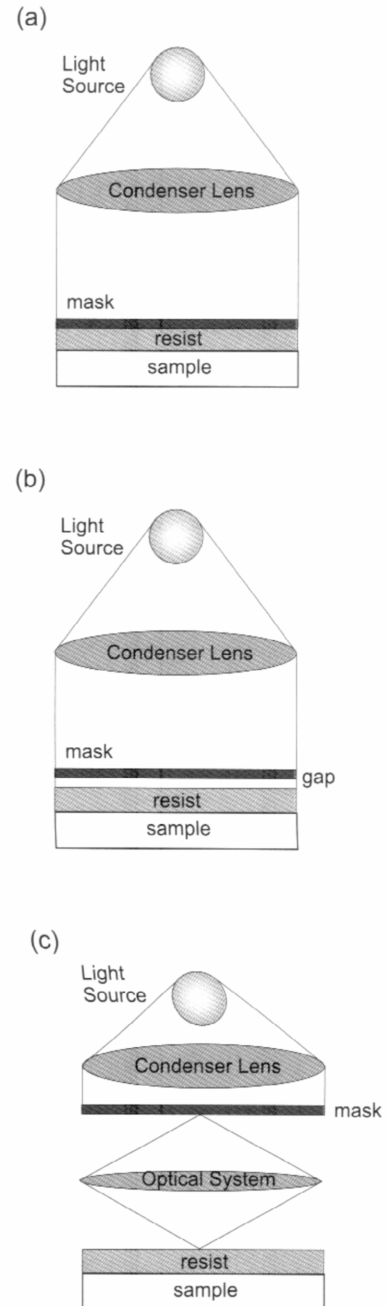


Figure 3: Lithography methods:
(a) contact,
(b) proximity and
(c) projection lithography.

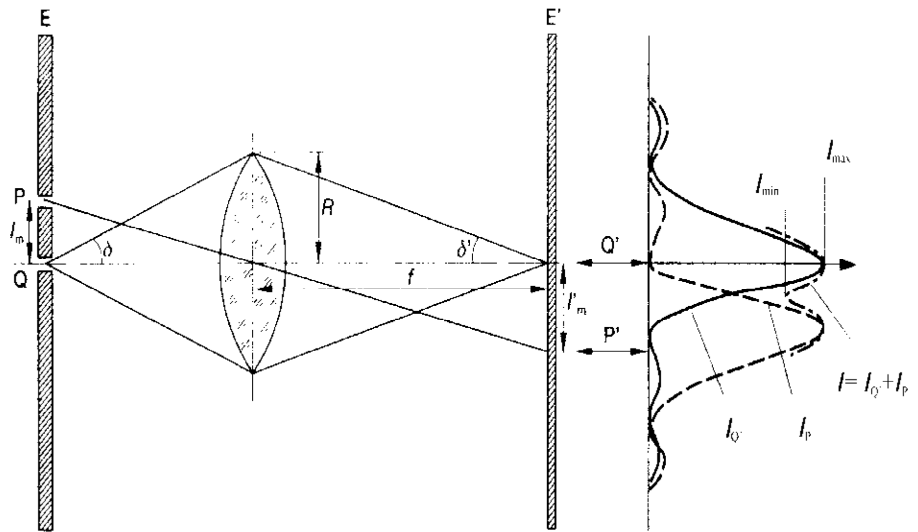


Figure 4: Intensity pattern of two features P and Q at projection lithography: The intensity distribution at the sample is broadened due to deflection [4].

Figure 4 clarifies the connection between mask, diffraction and intensity distribution in the image plane. Due to diffraction two sharp features, P and Q, on the mask give rise to an overall intensity distribution on the sample. To resolve these two features the intensity distribution has to have a minimum between the two main maximums. It is useful to define the so called modulation transfer function (*MTF*) as:

$$MTF = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} \tag{6}$$

The higher the value – the higher the difference between the maximum and minimum intensity – the better the contrast between exposed and unexposed areas, the better is the resolution of the equipment. It should be noted that the *MTF* is only derived by properties of the optical system. It is a measure of the capabilities of the lithographic tool in printing structures.

Resolution Enhancement

For a given tool and technology, the resolution is a given figure. There have been several attempts to improve this essential figure without any major changes to the tool (i.e. no other wavelength or *NA*). Figure 5 shows the possible places where changes can be made in the optical path to improve resolution. Two of these attempts are discussed in the next subsections, the phase shift techniques and off-axis illumination. In off-axis illumination, the effective light source is tailored, while in phase shifting techniques the wave edge of the illuminating light is tailored by the mask.

Phase Shifting Techniques

A huge improvement in resolution and/or in depth of focus can be obtained by improving the contrast by tailoring the phase differences of the wavefront. The phase difference is changed by varying the optical path length of the light passing through the vicinal structures, leading to constructive and destructive interference, which improves contrast (i.e. increase I_{max} or decrease I_{min}). To understand the method the approach proposed by Levenson in 1982 [26] is discussed.

Consider a lines and spaces structure with pitch $2p$. Figure 6 shows at the left hand side the amplitudes and intensities in the case of a conventional mask. At the mask itself, the normalized amplitudes are of rectangular shape (either +1 or 0) and give a proper image, but the light is diffracted into the dark regions and so the amplitude distribution is broadened as shown in Figure 6. The intensity of the light is the square of the sum of the amplitudes, so there is an intensity distribution with a significant I_{min} between the maximum intensities.

Now consider the case when the amplitudes of the light passing through the vicinal structures are out of phase by π (i.e. +1, 0 and –1) (Figure 6, right hand side). Again the light is diffracted into the dark areas, but now the light interferes destructively: There is a point where the sum of the amplitudes is zero, so the intensity is zero, too. These

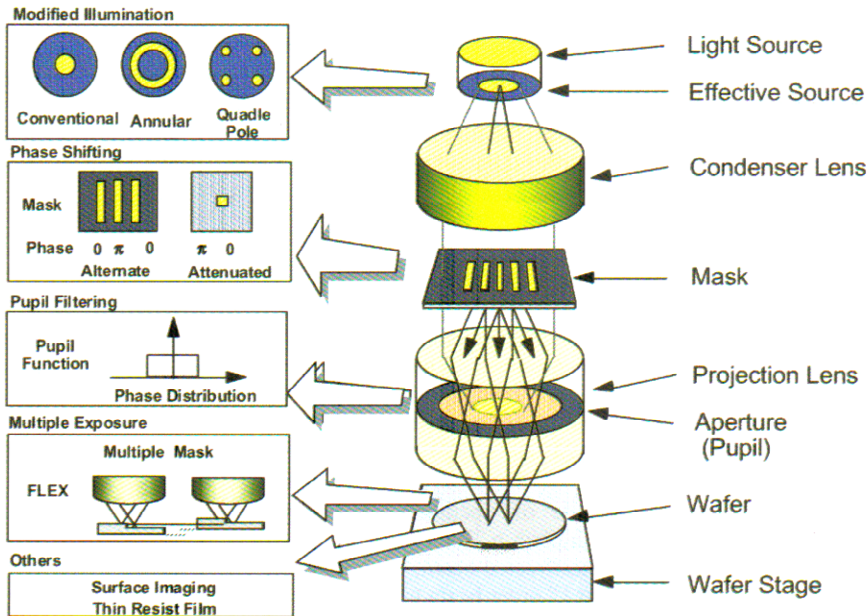


Figure 5: Survey of the resolution enhancement techniques.

so-called *Levenson* or *alternating phase shift masks* (PSM) can improve the resolution by 40 %. Unfortunately, this improvement is pattern-dependent; for a single structure there is no neighboring structure, so there is no light to interfere with. Even if there are structures which are not in a regular arrangement, there is no defined phase shift between these structures which could yield an improvement in the resolution of all structures.

The phase shift can be obtained by an additional transparent layer on the mask. If it has the refractive index n and thickness d, the phase shift is $\Phi = (n-1)2\pi d/\lambda$. So a shift of π is obtained, when the condition $d = \lambda/[2(n-1)]$ holds. On the other hand, it is also possible to recess the mask material so that the right optical path difference is obtained. But the etch depth can be controlled by the time only, and not, as in etching away an additional layer, by the thickness of the layer itself.

To deal with the drawbacks of alternating PSM, several other methods have been developed, which are described next. In rim-PSM, the whole mask is covered by a phase-shifter material and then with the resist. After development, the phase shifter is etched anisotropically and the masking layer is etched isotropically. By this a undercut under the phase shifter occurs at the rim of every structure. This also yields a resolution improvement, but not as much as with alternating PSM, although it is therefore not limited to certain structures.

Another way to engineer the optical path lengths is attenuated PSM. Here the opaque layer is replaced by a partially transparent (about 10 %) layer. The light passing these semi-opaque areas is not strong enough to expose the resist, by it can interfere with the light passing the transparent areas. So an improvement of resolution can be

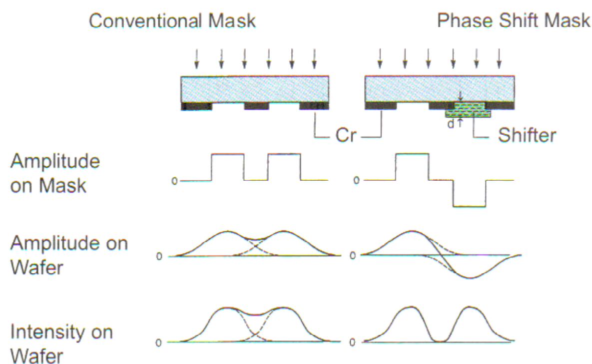


Figure 6: Comparison of the light amplitudes and intensities at the mask and on the wafer for a conventional and a phase shift mask. Note that the intensity on the wafer between the two features is zero for the phase shift mask [26].

obtained. The advantage of attenuated PSM is the easier mask processing. There is no extra layer as in alternating or rim PSM. The technology to process the semi-transparent layer is in principle the same as with a *normal* opaque layer.

PSM techniques were introduced in 1982, but only from 1999 they have been used for industrial production. An example which illustrates the impact of PSM methods is the results published by INTEL on the International Electron Device Meeting (IEDM) in 2000. A 248 nm phase-shiftmask lithography tool was used to produce a MOSFET with a 30 nm gate length [36].

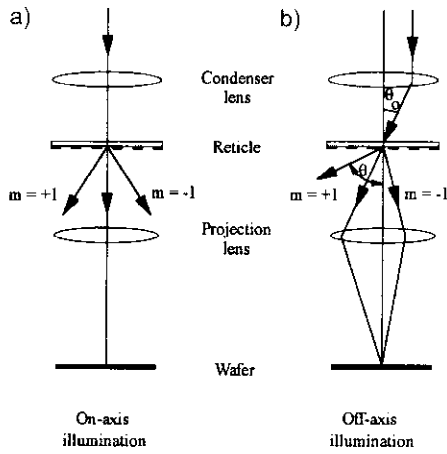


Figure 7:
(a) Optical path and deflection orders of on-axis and
(b) off-axis illumination. Note that with the same wavelength and structure size, the off-axis illumination allows the 1st order beam to pass the optical system [3]. A good description of off-axis illumination is also found in [6].

Off-Axis Illumination

To improve resolution without decreasing the wavelength or increasing *NA*, so-called off-axis illumination was applied. The method was already known as a contrast-enhancing technique for optical microscopes. With off-axis illumination, the light beam is directed from the mask towards the edge of the projection lens, and not, as in on-axis illumination, towards the center. In normal illumination with partially coherent light, there always is part of the light which is off-axis, but in the context here with off-axis illumination there is no on-axis component.

To understand the mode of operation of off-axis illumination, consider a line-and-spaces structure with pitch p. The incident light will be diffracted into a set of beams, of which only the undiffracted beam, the zero-order beam, travels in the direction of the incident light. The 1st order beam travels under the angle $|\theta_1| = \arcsin(\lambda / p)$. If p is too small, then $|\theta_{\pm 1}|$ is bigger than the acceptance angle α of the projection optics, then only the zero-order beam is projected to the sample (Figure 7a). But this does not carry any information of the pattern, and hence the pattern cannot be transferred onto the sample. At least the zero- and the 1st order beam have to be in the range of the aperture angle. If the incident light hits the mask under an angle $\Theta_0 < \alpha$ the undiffracted beam enters the projection lens at the edge, and the 1st order beam is still collected by the lens, and therefore a pattern transfer is still possible. The angle of incidence Θ_0 can be realized by inserting an aperture in the optical path between condenser and mask (Figure 7b).

Although the higher resolution is an advantage of off-axis illumination, the impact on the depth of focus (DOF) is of even greater value. In on-axis illumination, the beams of different deflection orders have to travel in different ways so they are phase-shifted to each other, which results in a lack of focus. In off-axis illumination, the zero order and 1st order beam reaches the projection lens at the same distance from the center, which means that their optical path length is the same. So the relative phase difference between these beams is zero, which increases the DOF dramatically.

Off-axis illumination is facilitated by an aperture (Figure 8) which is located in front of the condenser lens. It depends on the apertures shape which structures are improved. If there is an aperture as in Figure 8a, only the structures perpendicular to the arrangement of the apertures will be improved. The aperture shown in Figure 8b yields an improvement of structures which are adjusted to *good* angles – up/down or left/right direction. This is sufficient because in normal cases, the features are in a *good* arrangement. The aperture in Figure 8c even decreases this problem, but here the improvement in DOF is less.

When the resolution in principle has to be improved, then according to the Rayleigh criterion either the wavelength λ or the technology parameter k_1 have to be decreased, or the numerical aperture *NA* has to be increased.

Increasing *NA* means physically bigger lenses. Here the problem arises that it is difficult to produce huge lenses with the required quality; on the other hand the available materials also limit the physical size of the lenses. So there are still two possibilities of increasing the resolution: smaller λ and smaller k_1.

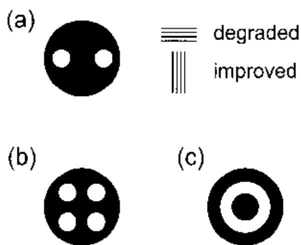


Figure 8: Apertures facilitating off-axis illumination.
(a) improvement of resolution perpendicular to the holes in the aperture,
(b) improvement in up-down and left-right direction, but not in diagonal direction and
(c) improvement in all directions [3].

2.2 Exposure Wavelength and Light Sources

Progress in optical lithography in the last few years was achieved by decreasing the exposure wavelength λ from 436 nm to 193 nm nowadays; research is in progress to push this boundary down to a few nm. In this section the different wavelengths, the methods of obtaining that light and the implications for the process are discussed. In Tab. 1 the wavelengths, the sources and the names of the wavelength ranges are given.

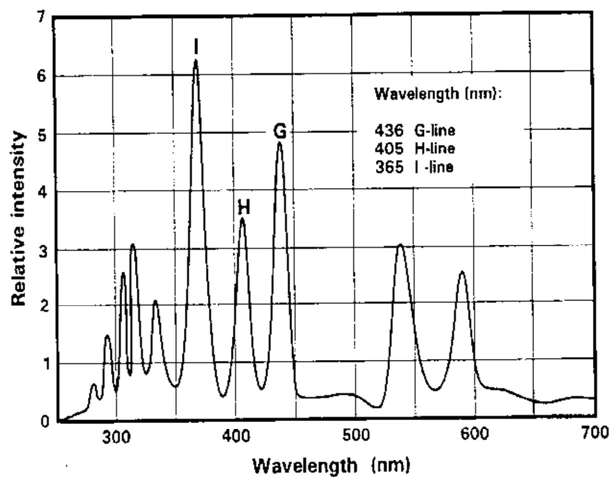


Figure 9: Spectrum of a high pressure Hg-lamp [46].

The first light used was the light emitted from Hg-arc lamps. It provides three lines, the G-line (436 nm), the H-line (405 nm) and the I-line (365 nm). A spectrum of a high-pressure Hg-lamp is shown in Figure 9. With typical k_1 and NA resolutions of ~400 nm were achieved. A further decrease of λ to 250 nm was obtained by a mixture of Hg and Xe, improving resolution to 300 nm, but the intensity at this wavelength is low.

To solve the intensity problem, at 250 nm a new light source occurs: the excimer laser. The word stems from *exited* and *dimer* and describes a molecule which only exists in an exited state. The gas mixture in an excimer laser is either KrF, ArF or F_2, resulting in the so-called deep UV (DUV) wavelengths of 248 nm, 193 nm and the vacuum UV (VUV) wavelength 157 nm, respectively. The excimer molecule consists of a noble gas and a halogen atom; in the ground state they cannot react, but if one or both are in an excited state, an exotic molecule can be formed. These dimer molecules decay into the ground state of both constituents with the emission of DUV light. The spontaneous decay time is long (i.e. nano- to microseconds), so inversion can be achieved by pumping the laser gas electrically.

In production DUV lithography with a resolution of 180 nm is used, while the boundary in research is being pushed down even further [36].

Wavelength [nm]	Source	Range
436	Hg arc lamp	G-line
405	Hg arc lamp	H-line
365	Hg arc lamp	I-line
248	Hg/Xe arc lamp; KrF excimer laser	Deep UV (DUV)
193	ArF excimer laser	DUV
157	F_2 laser	Vacuum UV (VUV)
~10	Laser-produced plasma sources	Extreme UV (EUV)
~1	X-ray tube; synchrotron	X-ray

Table 1: Illumination wavelengths, light sources and light ranges

Between 157 nm and ~13 nm is a huge gap where no usable wavelength exists. This is because all materials absorb light of that wavelength, so no masks, lenses and mirrors can be made. Nevertheless, when wavelengths in the range of 13 nm are used, it is possible to set up an optical path to do projection lithography. This range is called extreme ultraviolet (EUV). Shrinking the wavelength into the range of 1 nm leads to x-ray lithography. Here it is not possible to perform projection lithography because there is no material to set up an optical system (see Sec. 4).

The methods used to generate this light are the same for both ranges. All of them have to meet certain requirements such as being efficient enough at the desired wavelength and have low debris production (or feature a mechanism to avoid the contamination of tool and sample).

Firstly an x-ray tube can be used. In an x-ray tube, a metal anode is radiated with high energy electrons so that the characteristic x-ray radiation of the metal is emitted. The wavelength can be adjusted by the right choice of metal and electron energy. Unfortunately there are two drawbacks. On one hand, the intensity of these sources is very low leading to exposure times of several hours. This may match the requirements for research purposes, but surely not the ones of industrial production. On the other hand, the anode metal is sputtered and contaminates the exposure tool and the sample. This leads to unwanted loss of intensity, which decreases the lifetime of the tool and destroys the sample. In summary, x-ray tubes do not meet the requirements for EUV or x-ray lithography.

To a second group of methods the gas discharge sources belong. There are different types under investigation. While they differ in the concepts of plasma ignition, geometry of the source and discharge parameters, they all have in common that a plasma is generated by a fast discharge of electrical energy and emits thermal radiation in the EUV range. In common, gas discharge sources still suffer from debris. Nevertheless, in recent years some progress has been made with these issues [29], [30].

Another kind of sources is the laser-produced plasma sources (LPP). A pulsed laser focused on a target consisting of oxygen, fluorine, neon or xenon excites a plasma discharge in the desired wavelength region. The target is either solid (cryogenic), liquid or gaseous. The method is almost the same for all cases: The target is injected into a vacuum. Onto the jet a laser is focused, whereby the plasma is stimulated. The drawback is that the debris problem is not solved at all. For plasma excitation the gas has to have a certain pressure, therefore the distance between the plasma and the injector is too short so that the injector is sputtered. For liquid xenon targets [7] or a double gas target [8], which are under development, the debris problem is reduced. In a double gas target, the Xe-injector is surrounded by a second injector, from which a low-Z gas (He) is injected. The He encloses the Xe so that the distance between the injector and the plasma can be larger; therefore there is less debris and hence less contamination. Figure 10a shows a cross section of the injector, Figure 10b a space-integrated spectrum from a double-stream Xe/He target and Figure 10c the same for an ordinary Xe target.

The only light source which is luminous enough, at least in the 1 nm-wavelength range, and where no debris is produced is a synchrotron source. Electrons are accelerated onto a circular path and hence emit bremsstrahlung. But the synchrotron source is very expensive and therefore the cost of expanding lithography by one tool is very high. Also the shielding of the synchrotron is a drawback for these sources.

The question of which source will be used as an EUV or x-ray source is still not decided. While synchrotrons meet the optical requirements for wavelengths in the 1 nm-range, they are very expensive both with respect to purchasing costs and the clean-room space they require. X-ray tubes are suitable only for research purposes, while LPP offers a sufficient light quality for development, but not for production. Discharge sources still suffer from debris, but they are cheaper to purchase cost of ownership. Good comparisons between the different sources are given in [31], [32].

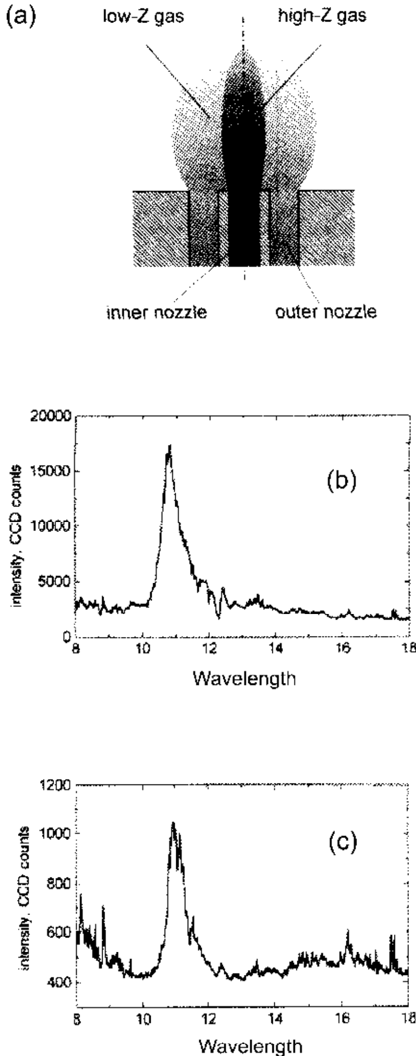


Figure 10:
(a) Double nozzle injector of a laser produced plasma source; through the inner nozzle the high-Z gas and through the outer nozzle the low-Z gas is injected; both gases form the target. Spectral distribution spectrum for the spectral image of
(b) a double stream Xe/He target and
(c) an ordinary Xe target [8].

2.3 Mask Materials and Optical System

2.3.1 Set-up of the Optical Path

It is possible to obtain light with wavelengths from <1 nm to 500 nm. But besides the light source supplying light of a certain wavelength, an optical system has to be set up to do lithography. Masks, mirrors and lenses are needed which are suitable for the used wavelength. This is expensive.

There are two concepts for setting up the optical system. On the one hand, it can be designed with refractive elements (e.g. lenses: refraction optics). In a refraction optics system, the light passes the mask and lenses. Therefore these components have to be made of transparent materials. But the transmission through the materials depends on the wavelength. While soda-lime glasses and borosilicate glasses were used in earlier IC fabrication, these glasses become too less transparent as the wavelength approaches 250 nm. Furthermore, these materials have a high thermal expansion coefficient ($\approx 93 \times 10^{-7}\,K^{-1}$), which leads to a significant expansion of the masks when it is heated by the absorbed light. Fused silica, used instead, is transparent enough for even 193 nm

7 Photoresist

Photoresists are also an integral part of lithography. The performance of the resist is the determining factor for the magnitude of the technology factor k_1. In general, photoresists are polymers which react when exposed to light. There are two different types of resists: With positive tone resists, the exposed areas of the resist will dissolve in the developer, with negative tone resists, the exposed areas will remain.

Positive tone resists consist of three components, a resin, which serves as a binder and establishes the mechanical properties, a photoactive compound (PAC), and a solvent to keep the resist liquid. The resin is not normally responsive to the exposure. The commonly used positive tone resist system for g- and i-line lithography is the novolac/diazonaphthoquinones (DNQ) system. The novolac is the resin material and dissolves in aqueous bases. The DNQ is the PAC, but when unexposed it acts as a dissolution inhibitor. Figure 22 shows the reaction cycle of the DNQ upon exposure. Upon exposure N_2 is split off the molecule. After a rearrangement, the molecule undergoes a reaction with the H_2O, which stems from the air. The reaction product now does not behave as a dissolution inhibitor, but as a dissolution enhancer. Therefore the exposed areas of the resist will dissolve about 100 times quicker than the unexposed areas.

Negative tone resists also consist of the three compounds: resin, photoactive compound and a solvent to keep the resist liquid. The resin consists of a cyclic synthetic rubber, which is not radiation-sensitive, but strongly soluble in the developer (non-polar organic solvents). The PAC is normally a bis-arylazide. Figure 23 shows the chemical structure of a rubber resin and a PAC. Upon exposure, the PAC dissociates into *nitrene* and N_2. These nitrene molecules are able to react with the rubber molecules, so a cross-linking between two rubber molecules can be established. Thus a three-dimesional cross-linked molecular network is formed, which is insoluble in the developer .

As device dimensions are scaled down further, the g-line steppers as well as the novolac/DNQ resists have been improved, so the features for 350 nm generation could be printed. But reaching the 250 nm generation, the illumination wavelength was shifted to 250 nm, too. However, at this wavelength novolac and DNQ do strongly absorb the light, therefore another class of resists had to be developed. Furthermore, the intensity of

the mercury lamps at 250 nm was very low, so a high sensitivity of the resist was needed. The so called chemically amplified resists (CAR) use a chemical reaction to improve sensitivity and they are compatible with a 250 nm exposure wavelength. In a CAR, one of the compounds is a photo acid generator (PAG). Upon exposure an acid is released by PAG. During the post-exposure bake (PEB) – a heating of the sample after exposure – this acid reacts with the resin so that, firstly, the resin becomes soluble to a developer, and, secondly, a new acid is released. With this catalytic reaction it is possible to get 500 to 1000 reactions from one photogenerated molecule (Figure 24). Positive and negative tone CARs are available.

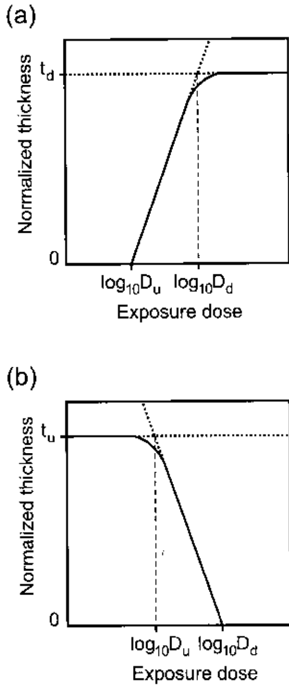


Figure 26: Schematic view of a contrast curve for (a) negative tone resist and (b) positive tone resist.

How do the resists affect the resolution? We have to consider the contrast of a resist: At what exposure dose is the resist exposed, and at what dose it is not yet exposed? As explained earlier, the light intensity at the sample is not of a rectangular shape, but is a diffraction pattern, so the resist at the sample is exposed according to that distribution. In Figure 25 a type of a contrast curve of a negative tone resist is given. In that curve, the etch rate of the resist in the developer is shown against the exposure dose. In an equivalent representation of the contrast curve, the normalized remaining resist thickness after a defined development process is plotted linearly against the logarithm of the exposure dose. For low exposure doses, the resist still behaves like an unexposed resist, for high doses it is fully activated. The transition between these two regions has to be steep to get a high contrast. To clarify this point refer to the intensity distribution of two patterns next to each other given in Fig. 4. The maximum intensity $I_{\max}$ has to be on the right side of the transition in Figure 25, the minimum intensity $I_{\min}$ on the left side.

The measure of the contrast is the contrast parameter γ. The higher γ the higher is the contrast, the closer $I_{\max}$ and $I_{\min}$ can be. It is determined as follows: The transition range of the contrast curve is fitted linearly the region where the resist is not etched by the developer (Figure 26a for negative tone resists, Figure 26b for positive tone resists). Where these two evens intersect, there is the dose D_u for positive and D_d for negative tone resists. The dose where the thickness of the resist becomes zero is D_d for positive and D_u for negative tone resists. The parameter γ is simply the negative slope of the contrast curve in the transition region on a logarithmic scale:

$$\gamma_{\pm} = -\frac{t_d - t_u}{\log_{10} D_d - \log_{10}(D_u)} = \frac{\pm 1}{\log_{10}\left(\frac{D_d}{D_u}\right)} \tag{7}$$

where t_d is the normalized thickness of the exposed resist, which means that t_d is 0 for positive tone resist and 1 for negative tone resist, and t_u is the normalized thickness for unexposed resist, so t_u is 1 for positive tone resist and 0 for negative tone resist; the sign stands for positive/negative tone resist, respectively. This characteristic can be expressed in terms of the so-called *critical resist modulation transfer function* $CMTF_{resist}$ which is defined as:

$$CMTF_{resist} = \frac{D_d - D_u}{D_d + D_u} = \frac{10^{\pm\frac{1}{\gamma}} - 1}{10^{\pm\frac{1}{\gamma}} + 1} \tag{8}$$

where the + stands for positive tone resist, and the – for negative tone resist. Now let us consider the exposure system with a given *MTF* with which a positive tone resist should be exposed. Choosing the exposure time s_e, with $I_{max} \cdot s_e = D_d$, $I_{min} \cdot s_e$ has to be less than D_u (otherwise $I_{\max}$ and $I_{\min}$ do not lie on the different sides of the slope of the contrast curve). Now :

$$MTF = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \cdot \frac{s_e}{s_e} = \frac{D_d - D_{\min}}{D_d + D_{\min}} \geq \frac{D_d - D_u}{D_d + D_u} = CMTF_{resist} \tag{9}$$

For a given *MTF* of the exposure system, the *CMTF* has to be smaller, and this means that the contrast of the resist has to be high enough.

Now let us consider the path of light in the resist. During exposure, the resist is not only traversed by the incoming beam, but due to reflection at the resist/sample interface, there are also reflected beams, giving rise to standing waves. The intensity variations emerging from these standing waves can be seen in the resist profile after development

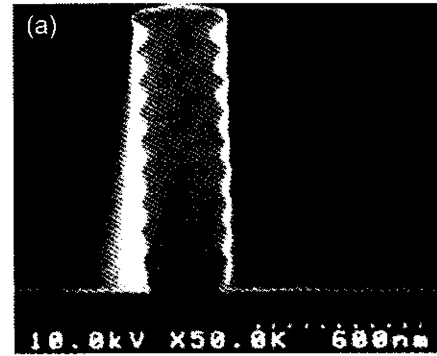
(Figure 27a) and degrade the resolution. With CAR these ripples in the resist can be abolished by a thermal treatment after exposure (i.e. during a PEB). The reacted photoactive complexes diffuse, smoothening the side walls.

Furthermore, the exposure is not independent of the sample itself. Figure 27b shows simulated values of the linewidth transferred into the resist for two different samples – silicon wafers with oxide layers differing by the oxide thickness. It is seen that the linewidth depends strongly on the resist thickness and on the nature of the sample. This phenomenon stems from the reflections at the oxide/silicon interface and at the resist/oxide interface. To prevent these influences, anti-reflex coatings (ARC) are applied. It is possible to apply an ARC before the resist (bottom ARC) or afterwards (top ARC). With the BARC the reflectivity of the resist/substrate interface and with the TAR the reflectivity of the resist/air interface is minimized.

There are two possibilities to achieve this aim for BARC. First, the BARC could show a high absorption of the incident light. Unfortunately, if the absorption is high, the reflectivity of the BARC/resist interface will increase, degrading the effectiveness of the BARC. The second possibility is to match the BARC thickness and the refractive index, so that the optical path length of the BARC is $\lambda/4$. If the sample is exposed, the incident beam hits the resist/BARC interface, and is partially reflected and partially transmitted. The transmitted beam transverses the BARC, is reflected at the BARC/substrate interface and travels back to the BARC/resist interface. This beam and the first reflected beam are out of phase by $\pi/2$, so they interfere destructively, and the reflectivity at the BARC/resist interface is reduced. The TAR also has an optical path length of $\lambda/4$, so the interferences of the reflected beams are destructive.

BARC materials depend on the illumination wavelength and the samples. Spins on BARCs are primary absorption-type and consist of polymers. Oxinitrides deposited by PECVD can be used for index-matching type BARCs. The BARC layer has to be developed after lithography, requiring an additional process step. Figure 28a shows a resist structure without, Figure 28b with a BARC.

TAR can be spun on after spin coating. After exposure the TAR can be removed before development. Some TARs are designed to be developed in aqueous-based developer solution, which does not affect the resist. The handling of these TARs are much less complicated than the handling of BARC.



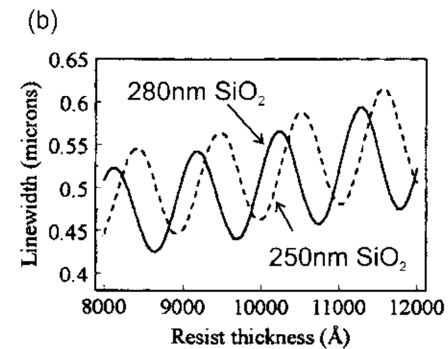


Figure 27:
(a) Impact of standing waves on the developed resist.
(b) Simulated linewidth as a function of resist thickness and substrate [3].