Low Pressure Plasmas and Microstructuring Technology

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To my wife

Preface

Over the last forty years, plasma supported processes have attracted ever increasing interest, and now, all modern semiconductor devices undergo at least one plasma-involved processing step, starting from surface cleaning via coating to etching. In total, the range of the treated substrates covers some orders of magnitude: Trenches and linewidths of commercially available devices have already passed the boundary of 100 nm, decorative surface treatment will happen in the mm^2 range, and the upper limit is reached with surface protecting layers of windows which are coated with $\lambda/4$ layers against IR radiation.

The rapid development of the semiconductor industry is inconceivable without the giant progress in the plasma technology. MOORE's law is not carved into stone, and not only the ITRS map[1] is subject to change every five years but also new branches develop and others mingle together.

Moreover, the quality of conventional materials can be improved by plasma treatment: Cotton becomes more crease-resistant, leather more durable, and the shrinking of wool fibers during the washing process can be significantly reduced.

To cut a long story short: More than 150 years after the discovery of the sputtering effect by GROVE, plasma-based processes are about to spread out into new fields of research and application [1]—no wonder that the market for etching machines kept growing by an annual rate of 17 % up to the burst of the internet bubble, and it took only some years of recovery to continue the voyage [2].

To realize a multi-color flat panel display measuring 16 square feet, a total of 300 000 LEDs is required. 1994, just in front of the launching of the blue LED, the fraction of LEDs (which effectively emit in the visible range) amounted to about $^1/_3$ of the total compound semiconductor market of $4.4 billion. Four years later, the fraction of so-called high-brightness LEDs had been grown by 64 % (total market 1997: $7.1 billion), and the number of substrates which were subject to epitaxial processes to produce LEDs had been increased by almost 300 % (Fig. 1). This was conservatively updated to an estimated amount of

[1] **I**nternational **T**echnological **R**oadmap for **S**emiconductors

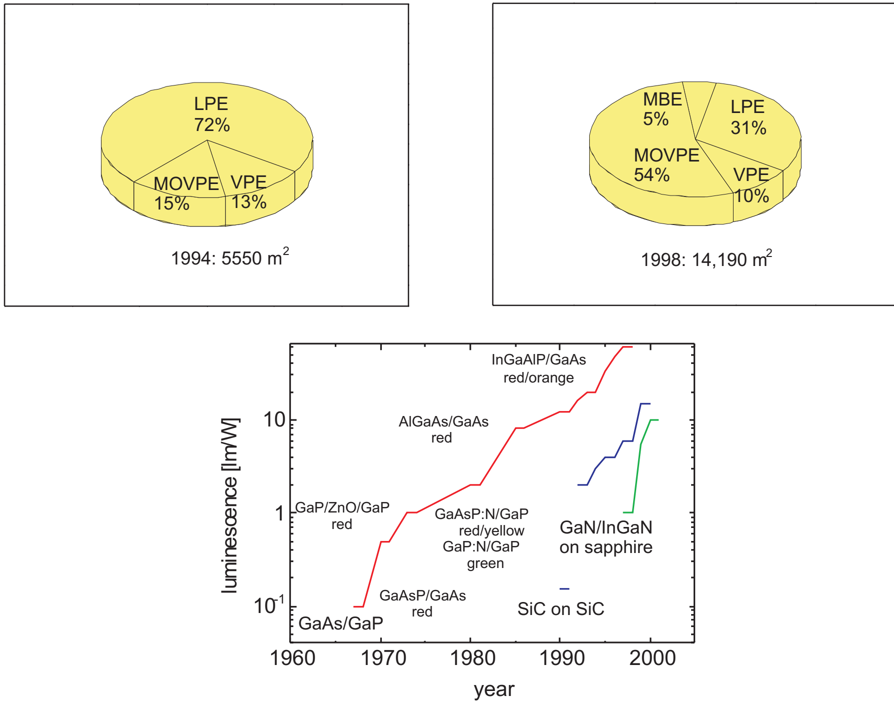


Fig. 1. From 1994 to 1998, the area which had been epitaxially grown for LEDs rised by about 300 % from 5 550 m^2 to 14 190 m^2 (about $1^1/_2$ soccer pitches). Simultaneously, the main interest moved from relatively simple techniques (liquid-phase epitaxy) to highly sophisticated gas-phase epitaxy. The etching techniques covered the whole palette from sewing via wet etching up to dry etching methods, and here from hard gunfire by an argon ion beam to subtle etching by generating a reactive plasma of high density but consisting of ions with relatively low energy. This is associated with a steep increase in colorful brillance or efficacy.

$1 billion in 2003 [3]. Despite the deep crisis which was even aggravated by the assassination on Sep 11, the market had recovered. Alone the market for high-brightness LEDs has hit the volume of the total LED market of 1997 [4] (in numbers of LEDs shipped: 20 billion units in 2004, 30 billion units in 2006), and the next landmark has been reached just now: Almost every third LED is used for automotive purposes, most of them belong to the category high-brightness [5]. (Figs. 2).

Progress is made most obvious by a flashback. In 1978, the costs for a complete wafer fab amounted to about $20 mio., the narrowest geometries were about 2 and 3 microns, and the yield remained at ridiculous 10 %. Some statements from the first number of *Semiconductor International* from the year 1979:

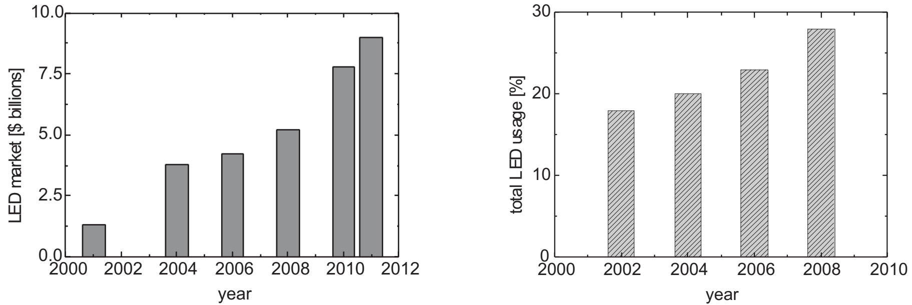


Fig. 2. 2007, the market for LEDs alone has hit the total volume of III/V compound semiconductors of 1997. In particular, the market for automotive LEDs has grown by more than 30 % in the last five years. By the end of 2008, almost every third LED is expected to be part of an automotive illumination with a growing fraction of high-brightness LEDs [4] [5].

- Progress in the area of photoresist and masks provided, deep-UV lithography will be the next technological step [6].
- Plasma etching will become a very important technology for pattern transfer, and plasma deposition shows the same auspicious propects . . . [7].
- Many of the problems what design is concerned can get over provided
  - a less efficient chip is accepted by the market,
  - test functions are integrated on the chip,
  - which is synonymous not to strive for the highest packing density [8].

This was 1978 [9]:

- minimum of the structures by about 2.5 μm;
- the design was at a maximum of eight masks;
- clean room class between 100 and 1 000;
- first application of steppers for processing of 4" wafers;
- gate electrodes with doped polysilicon;
- first operation of lasers for annealing purposes;

- minimum gate oxide thickness: 100 Å;
- wet etching still dominates, plasma etching as high-end technology is operated only in areas where undercut is not tolerable.

For the public, the computer market was entirely dominated by dinosaur computers, but the first programmable calculators were offered by Hewlett-Packard and Texas Instruments, the overwhelming part of light was generated by EDISON' evanescent bulb, and "cold light" was just a dream of some scientists.

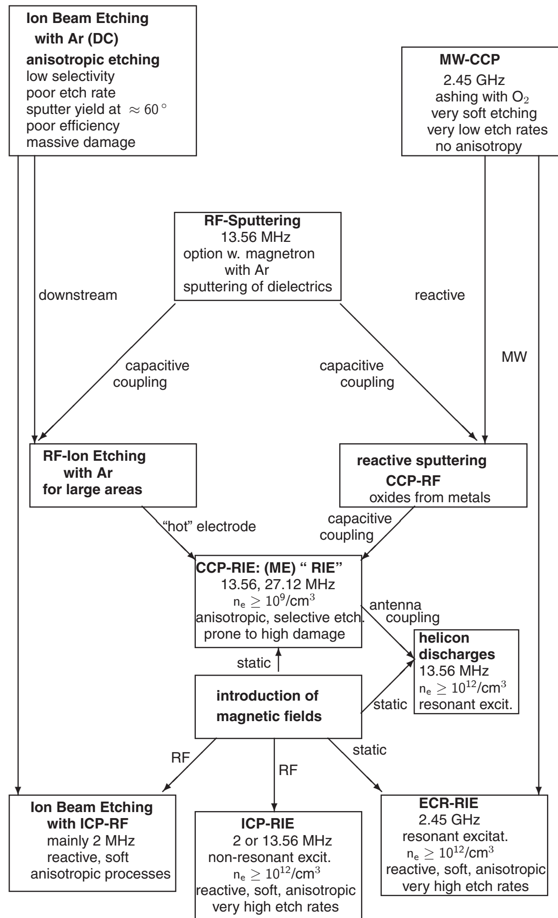


Fig. 3. Flow Diagram for Mutual Development of Excitation Methods and Reactive Processes

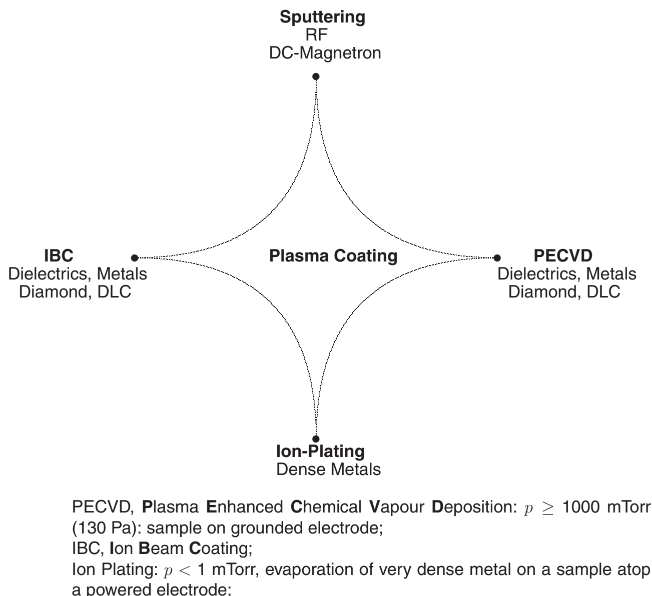
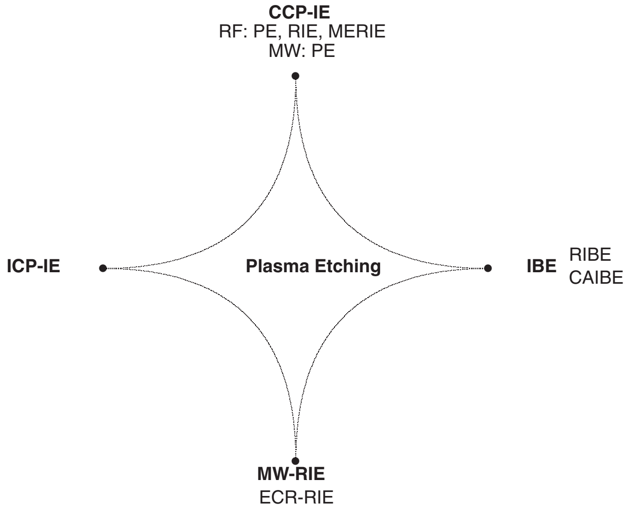


Fig. 4. Various dry etching methods. They mainly differ in the excitation method.

Today, the line widths of the most advanced devices are less than 1 000 Å, but the main issues in nanometer devices are still the patterning of the gate (MOS devices) or the mirror or facet (semiconductor lasers). The end of the common planar technology although further miniaturized is predicted to be reached by less than a decade. But perhaps the prognostic power will be comparable with the score of the prognosis for the world-wide oil deposits which should be depleted always "in the next fifteen years", who knows?

Therefore, we consider to address again a broad readership for the next edition of this book. After a short phenomenological introduction, the various methods to generate charged carriers are extensively discussed, keeping in mind that low temperature plasmas have been subject of intense research for now more than a century which comprises the methods to characterize the plasmas. In the second half, the technological techniques of surface refinement are discussed in two lengthy chapters, and we become again aware of the mutual challenges of surface treatment and plasma technology. Detailed derivations are compiled in a special chapter, including the detailed but tedious algebra. It has become customary to spell acronyms which are introduced just recently in capitals which are gradually transformed to small letters, and it is a matter of taste to decide whether this time is already passed by. Since this book is mostly directed to plasma beginners, I preferred to apply capitals throughout.



CCP, **C**apacitively **C**oupled **P**lasma;
ECR, **E**lectron **C**yclotron **R**esonance, downstream;
ICP, **I**nductively **C**oupled **P**lasma, downstream;
MW, **M**icro **W**ave (2.45 GHz);

PE, **P**lasma **E**tching: $p > 75$ mTorr (10 Pa): sample on grounded electrode;
IE, **I**on **E**tching,
RIE, **R**eactive **I**on **E**tching: $p < 50$ mTorr (7 Pa), sample on powered electrode;
IBE, **I**on **B**eam **E**tching;

MERIE, **M**agnetically **E**nhanced **R**eactive **I**on **E**tching: RIE; electrons are suppressed to reach the sample's surface by means of a magnetic field;
CAIBE, **C**hemical **A**ssisted **I**on **B**eam **E**tching;
RIBE, **R**eactive **I**on **B**eam **E**tching.

Fig. 5. Various dry coating methods. They mainly differ in the excitation method.

It is simply impossible to name all the collegues who discussed certain issues extensively or courteously passed me figures and micrographs (cf. Chap. 15). For more than a decade, I am now used to meet most of them during the annual conference of the AVS, feeling the reality of the scientific community. But in particular, I would like to thank Peter Awakowicz, Rod Boswell, Francis Chen, John Coburn, Vince Donnelly, Demetre Economou, David Graves, Michael Klick, Michael Lieberman, Ivo Rangelow, and Peter Unger.

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Munich, January 27, 2009 Gerhard Franz

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1 Introduction

From everyday life, we are familiar with discharges; consider atmospheric discharges which we observe in the form of lightning, and which equalize potential differences of some millions of volts within milliseconds. Very high temperatures can be generated with electric arcs, which were described for the first time by Humphry Davy in the year 1813. Two years later, they were applied to melt and fuse refractory metals [10]. The temperatures are 4 700 K at the electrodes and up to 7 000 K in the arc itself. With increased current densities, temperatures of up to 50 000 K could be reached. These are the surface temperatures of blue-white glowing O-stars (our sun, a G-type, has a surface temperature of about 6 000 K [11]).

Bushels of pink-purple sparks can be seen at sharply pointed structures (ship masts or spires) during thunderstorms. This electroluminescent coronal discharge is well known as *St. Elmo*'s fire. It was Benjamin Franklin who in 1749 proved this phenomenon to be electric in nature.

Glow discharges occur in diluted gases (low pressure discharges) at small current densities; they are used in sodium vapor lamps and fluorescent lamps; the former replaced normal incandescent lamps for street lighting from the 1960s, the latter still characterize the nightly atmosphere of famous places (*e. g.* Piccadilly Circus or Times Square).

A short glance in the Encyclopædia Britannica, and we find under "glow discharge": Self-sustained gas discharge with cold electrodes, and "discharge" itself means the evening out of various potentials.

A very simple glow discharge can be generated by fusing two electrodes into a glas tube (the typical Geissler tube tube has a length of about 50 cm) with a pumping-port. When we start evacuating the tube and simultaneously apply a voltage of about 10 kV, we will recognize a light apparition in the tube below a pressure of some Torr (some hundreds of Pa). We see a glowing serpent between the electrodes which enlarges its cross section with further falling pressure until it fills the whole cross section of the tube.

At pressures below about 1 Torr (1 kPa), the Crooke's or Hittorf's dark space appears in the area adjacent to the cathode, whereas glowing zones appear in the rest of the tube. Further decrease of pressure causes the dark space to grow until it fills the whole tube at pressures around 10 mTorr (1 Pa). Now, the greenish fluorescence of the glass tube remains as the last glowing apparition.

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The gas itself is partly ionized, its degree of ionization is typically some tens of ppm or $\leq 10^{-4}$. At a neutral density of $10^{14}\,\mathrm{cm}^{-3}$ or at a pressure of some mTorr ($^1\!/_2$ Pa), this would mean a charge density of less than $10^{-10}\,\mathrm{cm}^{-3}$ (sum of electron density and ion density, which must always be of equal size).

In 1928, it was LANGMUIR who denoted *plasma* a gas which is ionized to a large extent [12], and therefore, its charge density is called plasma density. In this nomenclature, this plasma will fall into the category tenuous plasma or low-density plasma. It conducts electric currents and can easily be influenced by external electric or magnetic fields. On the other hand, the plasma bulk will remain neutral, and this state is denoted quasineutral.

It is the simultaneous occurrence of long-range and short-range forces which distinguishes a plasma from a neutral gas, which can be described, at least in principle, with the kinetic gas theory and the corresponding refinements (various potentials of interaction to take into account short-range forces). Both types of matter have some properties in common; among them is the chaotic behavior of their constituents: The neutrals and charged particles move on randomly scattered trajectories.

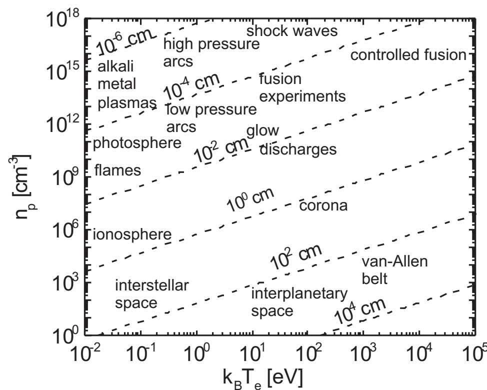

Fig. 1.1. Electron density in cm^{-3} for various plasmas as a nction of the electron temperature in eV. The straight lines are the DEBYE lengths.

Since the plasma density continuously diminishes by loss mechanisms such as recombination within the plasma and diffusion out of the glowing plasma volume with subsequent wall reactions, an external power source is required to keep a state of equilibrium. This source can be thermal in nature (flame or stars) as well as electric (gaseous discharge) or radiative (ionosphere).

Plasmas are stable within an enormous pressure range beginning at 10^{-4} Pa in the ionosphere ($120-400$ km height), 0.1 μbar (0.01 Pa) in ion beam sources, up to 10^{11} bar in the interior of the stars (Fig. 1.1). Since the 1950s, there have been tremendous efforts to keep plasmas stable in nuclear fusion systems.

The discharge pressure predominantly determines the properties of the plasma and hence its applications via the mean free path *(MFP).* Some examples are:

- Geiger-Müller counter ($p \approx 100$ mbar).
- Glow lamps (1 mbar $-$ 30 mbar).
- Fluorescent lamps (0.01 $-$ 1 mbar).
- Plasma ion sources (1 μbar $-$ 1 mbar).

In these few paragraphs, we have introduced several important properties for the understanding of a plasma. For the generation of carriers, some electrodynamical theories have to be applied to understand the creation of electric and magnetic fields in the plasma tube, whether they are static or time-dependent, and second how the single electron will respond to the action of these fields. Therefore, the point of view will vary between continuum theory and focus on a single particle, especially when collisions between particles are concerned by which carriers are generated and by which the energy which has been gained by the electrons will be dissipated into the plasma.

Because collision phenomena are essential in plasmas but disturb the didactic track from introducing phenomena and explaining them in an inductive way to eventually reach a state of comprehensive view, they are placed at the beginning of this treatise.

2 Collisions and cross sections

Elastic collisions are of paramount importance for OHMic heating and energy dissipation into the plasma; inelastic collisions are responsible for all the electronic excitation processes. For both processes, the deductive approach is chosen. By electronic and ionic impact, electrons can be released from surfaces; this process is required for the carrier avalanche in DC discharges, but has regained interest for stabilizing processes in production reactors whose inner surface is subject to various (mostly unintended) coating reactions.

2.1 Introduction

Plasmas are chaotic gaseous systems which contain electrically charged carriers and which maintain themselves by collisions of electric carriers with neutrals. These impacts lead to further carriers, but other energy-consuming processes, such as optical transitions, can be triggered as well. These collisions are subsumed as *inelastic.* Nearly all of the gaseous ionizations are due to collisions between slow heavy particles and rapidly moving electrons. If an electron falls short of the required kinetic energy to excite a heavy particle (atom or molecule), it can but exchange momentum with its counterpart, and we denote this process an *elastic* collision.

This process dominates all other possible collisions since only a very small fraction of electrons have kinetic energies which exceed the threshold of excitation. However, due to the unfavorable mass ratio of individual neutrals/ions over electrons, only a very small portion of energy is exchanged. The lack of efficiency causes an athermal plasma (Chap. 3): Electrons and heavy particles (sometimes even ions alone and neutrals alone) are in separate thermal equilibrium, and the temperatures differ tremendously.

In the case of electron trapping by a neutral molecule or ion, respectively, the electron density is reduced. This process is denoted electron attachment; it will become effective beyond pressures of about some Torr. Below this limit, diffusion processes dominate the loss of electrons: The particles exhibit random walks, caused by stochastic collisions. When the reactor wall becomes a partner of a collision process, the charge is terminated.

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With elastic collisions, only a very small fraction of kinetic energy is exchanged between particles which significantly differ in mass, which leads to only a small increase of kinetic energy of the translational energy of the gas constituents, i. e. a small rise in gas temperature. The electron kinetic energy is significantly reduced by inelastic collisions, which cause excitations of molecular rotations, vibrations and eventually electronic transitions. It is this excitation which generates ions, radicals and other dissociation products; furthermore, metastable species can be formed. When these inelastic collisions are possible, they dominate all other processes because of their large losses of energy. All these species can again react among themselves, but they can also relax. An electronic transition is often combined with radiation of light (UV/VIS range), which is specific to the ambient conditions (cf. Chap. 9).

Our interest in these processes is twofold: Elastic scattering is mainly responsible for energy transfer and dissipation of energy; by inelastic scattering, optical levels can be occupied or neutrals are excited to ions, and electrons are generated. For electron generation, we distinguish between certain classes which are denoted primary processes, i. e. thermal emission and field emission, and secondary processes:

- Generation of secondary electrons at the cathode and the walls by particles abundant in energy (γ-reaction): photons, electrons incident to the anode, ions incident to the cathode.

- Ionization by impact by particles abundant in energy in the negative glow and the dark spaces of either electrode (impact by electrons: α-reaction, impact by ions: β-reaction).

Primary processes can be neglected in glow discharges. Ions are produced only by gaseous reactions; otherwise, they can be generated by thermal emission, however, with very low yield [13].

2.2 Elastic collisions

2.2.1 Cross section

In an approximation to first order, the cross section for elastic scattering is adapted from kinetic gas theory, which regards molecules as hard spheres, and its fourfold area is defined as the cross section; we begin with the relation between mean free path λ and particle density n

$$\lambda \approx \frac{1}{n\sigma}. \tag{2.1}$$

The channel of a molecule with cross section σ as inner diameter is now exposed to an electron beam with flux I_0, which is shot into an ensemble of

non-interaction particles. After having covered a certain distance x, the flux has been attenuated to

$$I = I_0 e^{-\mu x} \tag{2.2}$$

according to BEER and LAMBERT with μ a reciprocal length which can be interpreted as mean free path λ following Eq. (2.1)

$$\frac{1}{\lambda} = n\sigma \tag{2.3}$$

with n the density of the molecules and σ the cross section of the specific interaction. For a fundamental understanding of the cross section, the integral attenuation of an electron beam, its angular and eventually its energetic dependence are required.

2.2.1.1 Cross section and mean free path in kinetic gas theory. The time τ between two collisions is of the order of $\tau \approx \lambda / < v >$ with $< v >$ the mean thermal velocity. The mean free path λ itself depends on particle density n and cross section σ according to Eq. (2.3) because it roughly scales with the target area of the molecule. In the simple approach of kinetic gas theory, this cross section is the only one considered and is the cross section for elastic scattering (see [14]). In this approximation, the cross section for elastic scattering is independent of temperature (energy) and is tabulated in units of πa_0^2—the cross section of the hydrogen atom with a_0 BOHR's radius (0.529 Å), $8.82 \times 10^{-17}\,\mathrm{cm}^{-2}$ [sometimes the averaged collision number P_c across 1 cm for a gas at 1 Torr (133 Pa) and 0 °C is found; the relation is $\sigma = 0.283 P_c$ in Å^2]. A typical value for λ is 4.5 cm for nitrogen at 1 mTorr (0.2 Pa).

In fact, the cross section weakly depends on temperature (kinetic energy): With decreasing temperature (reduced molecular speed), it rises slowly due to prolongation of the interaction. For example, by reducing the temperature by 200 °C from +100 °C to −100 °, σ_{el} rises by 30 % for nitrogen and oxygen.

2.2.1.2 Cross section and mean free path in plasmas. This temperature dependence is caused by weak intermolecular forces (polarization), which exhibit a weak r^{-6} dependence for the attractive part of the LENNARD-JONES potential Φ_{LJ}. In plasmas, however, we have bare charges which lead to intense, far-reaching interactions which can be described analytically only in some simple cases. To begin with, we introduce some experimental details for atoms and electrons:

- Atoms
  - In a sputter system operated with argon at 50 mTorr (7 Pa), the mean free path of the argon atoms is approximately 1.54 mm (25 meV Ar, $\sigma_{tot} = 26$ Å^2).

- Ions
  - The mean free path of ions is considerably smaller. λ for Ar^+ ions of medium velocity in argon at 30 mTorr (4 Pa) and 4 eV is about 0.87 mm and rises for 10 eV ions to 1 mm and for 100 eV atoms to 1.4 mm.
  - In ion beam sources which are driven at significantly lower pressures, they are larger by orders of magnitude: For 400 eV Ar^+ ions and a gas pressure of 10^{-4} Torr (13 mPa), λ equals 51.6 cm.
- Electrons
  - λ_e of fast electrons in argon [16 eV, which is at the maximum of σ (26 Å^2)] amounts to about 2.5 mm at a pressure of 50 mTorr (7 Pa), corresponding to about 7.5 mm at 20 mTorr (3 Pa).
  - Slower electrons ($E_{kin} \approx 4$ eV) with a smaller σ (9.7 Å^2) show a longer λ_e (at 20 mTorr about 13 mm) which applies also to rapid electrons (λ_e for 100 eV electrons is about 75 mm at 20 mTorr in argon). The frequencies for elastic collisions between electrons and neutrals yield, according to $\nu_m = n\sigma v$:
    * for 1 Torr (133 Pa, 3.54×10^{16} cm^{-3}) 3.8×10^9 s^{-1},
    * for 100 mTorr (13.3 Pa) 382×10^6 s^{-1} and
    * for 10 mTorr (1.3 Pa) 38×10^6 s^{-1}.

2.2.2 Definitions

First, we consider a beam of monoenergetic particles orientated in a parallel direction with respect to the x-axis and exhibiting a flux of N particles per cm^{2}sec (Fig. 2.1).

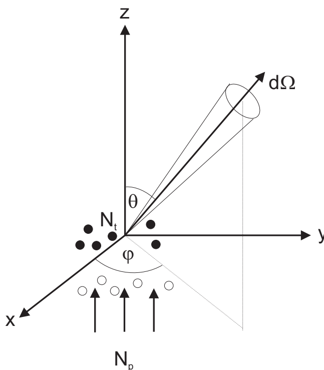

Fig. 2.1. Definition of the differential cross section. N_p projectiles collide with N_t targets and are deflected into dΩ, the differential solid angle element.

In the case of hitting an annular target with area $2\pi b\,\mathrm{d}b$ (b: inner diameter, $b + \mathrm{d}b$: outer diameter), we define the *differential scattering cross section* for solid angle $\mathrm{d}\Omega = 2\pi \sin\vartheta \mathrm{d}\vartheta$:

$$\frac{\mathrm{d}\sigma(v,\vartheta)}{\mathrm{d}\Omega} = \frac{b}{\sin\vartheta}\frac{\mathrm{d}b}{\mathrm{d}\vartheta}, \tag{2.4}$$

and the total cross section ("c" for collision)

$$\sigma_{\mathrm{c}}(v) = 2\pi \int_0^{\pi} \frac{\mathrm{d}\sigma(\vartheta)}{\mathrm{d}\Omega}\mathrm{d}\Omega, \tag{2.5}$$

which, in turn, does not allow any statement of the angular dependence. Furthermore, we define the frequency of collision according to

$$\nu_{\mathrm{c}}(v) = n\sigma_{\mathrm{c}}(v)v, \tag{2.6}$$

the mean free path again, but decorated with a subscript "c"

$$\lambda \approx \frac{1}{n\sigma_{\mathrm{c}}(v)} \tag{2.7}$$

and the probability of scattering

$$P_{\mathrm{m}} = \frac{1}{p\lambda}. \tag{2.8}$$

The change of momentum is in the center-of-mass system (Fig. 2.2):

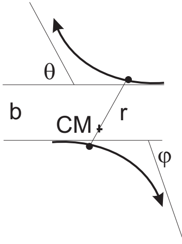

Fig. 2.2. Collision between two spheres in the center-of-mass system. b: scattering parameter, θ, φ: scattering angle, CM: center of mass.

$$\Delta\boldsymbol{p} = m\boldsymbol{v}(1 - \cos\vartheta) : \tag{2.9}$$

Collisions in the forward direction are minimally weighted ($\cos 0° = 1$), those in the backward direction ($\cos 180° = -1$), however, are considered most prominent: The diffusion is slowed down most effectively by collisions which are orientated backwards.

For the treatment of the transfer of energy and momentum, the most important property is the cross section for momentum transfer, which is $\sigma_{\mathrm{c}}(v)$, but weighted by the factor $1 - \cos\vartheta$: