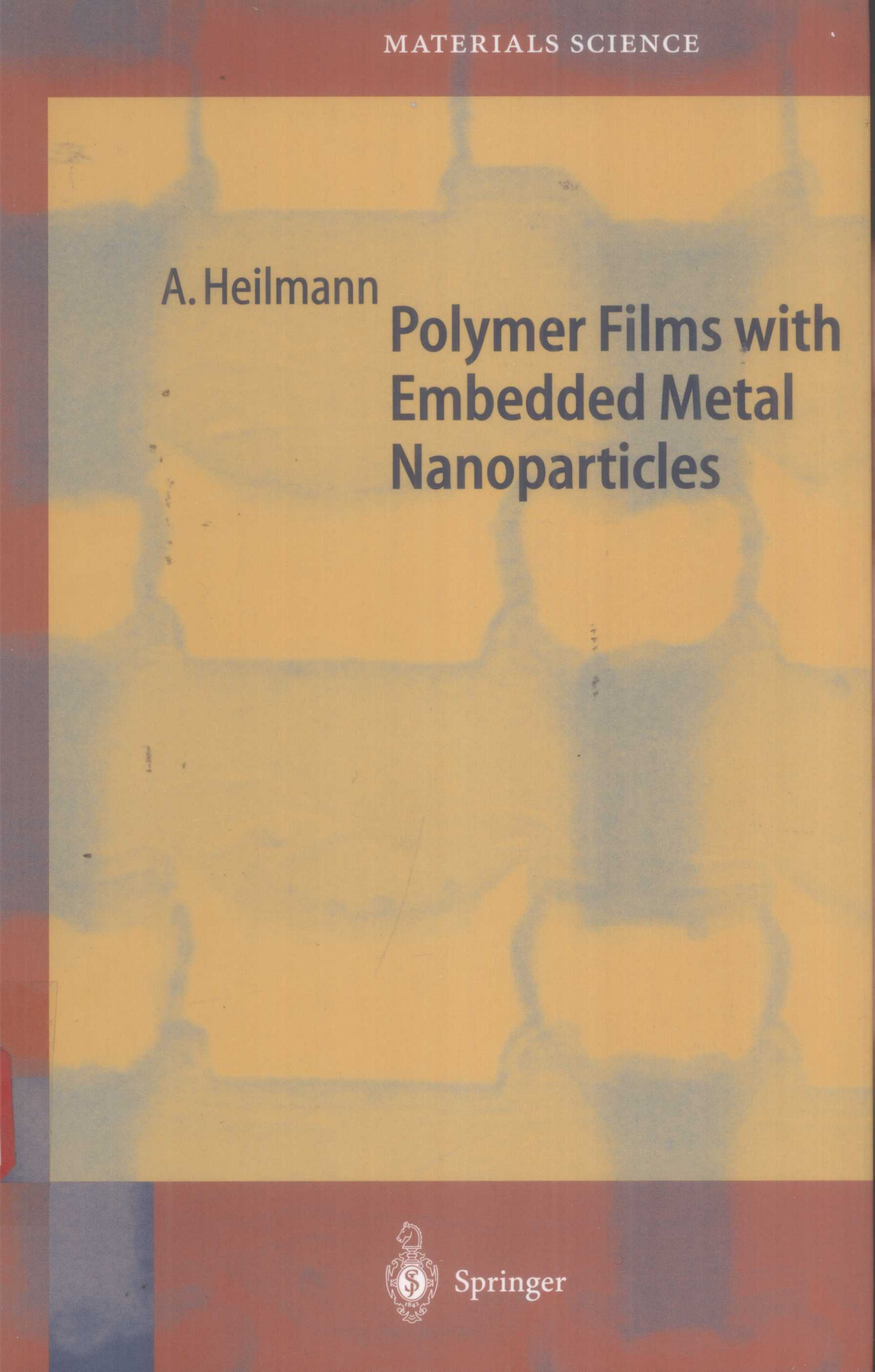

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Polymer Films with Embedded Metal Nanoparticles

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With 106 Figures

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Preface

Die Neigung des Menschen,
kleine Dinge wichtig zu nehmen,
hat sehr viel Großes hervorgebracht.

The human tendency
to regard little things as important
has produced very many great things.

Georg Christoph Lichtenberg (1742–1799)

The German physicist and poet Lichtenberg knew nothing about polymer films or nanoparticles. But it is quite likely that he had seen colored glasses with embedded metal nanoparticles made by unidentified Roman glassmakers or so-called ruby glasses created by Johann Kunckel (ca. 1630–1703), a German alchemist. Colored glasses were one of the first nanoparticle-containing materials designed by man. Kunckel did not have the equipment to investigate the structure of the material he had created and could not know that the deep purple color was a result of embedded gold nanoparticles.

These days, however, we have excellent tools such as electron microscopes for the determination of small structures with dimensions in the nanometer range. It is now well-established that such small particles have physical and chemical properties that are very different to those of the bulk material. Indeed an exact knowledge of the nanostructure and of its relation to the physical properties turns out to be essential for the design of nanostructured granular materials and for their industrial application.

It is this requirement that provided the motivation for this book. The aim is to present a detailed study of the correlation between nanostructure and physical (optical, electrical) properties. Due to the great variety of nanoparticle-containing materials, this study can only be performed by focusing on a selected class of materials. These materials are polymer thin films with embedded nanoparticles deposited by vacuum processes. This choice was made for several reasons. Firstly, films prepared in this way display a great variety of very different nanostructures and physical properties. Secondly, the nanostructure and the physical properties can be investigated without extensive sample preparation. Furthermore, these films can be used to investigate the processes taking place during thermal treatment, laser or electron irradiation. All these treatments can result in changes of the nanostructure. A final reason is the enormous application potential of such films in thin film technology. Hence, the aim of this monograph is to describe the detailed determination of the nanostructure of thin polymer films with embedded nanoparticles and its correlation to the optical and electronic properties. The vacuum deposition of polymer films was carried out by a low-temperature chemical vapor deposition process, referred to as plasma polymerization. Incidentally, Lichtenberg was also one of the first scientists to explore plasma processes.

The book was conceived with the intention of making experiments and theoretical considerations easily comprehensible and of allowing the methodological pathways to be easily transferred to other materials with similar nanostructures.

Many individuals have contributed ideas, suggestions, and experimental work which appear in this book. I express my gratitude to Eric Kay and James E. Morris who encouraged me to write this monograph. I wish to acknowledge Claus Hamann, Volkmar Hopfe, Dieter Gerlich, Uwe Kreibig and Dieter Katzer for their encouragement during recent years. I am also grateful to Andreas Kiesow for his experimental contribution and for a critical reading of the manuscript. Further experimental contributions were made by, among others, Jens Werner, Do Ngoc Uan, Wolfgang Grünewald, Michael Quinten, Anne Müller, Falk Müller, Frank Homilius, Mike Gruner, Dirk Schwarzenberg, and Nico Teuscher. Sincere thanks go to them all. Last but not least I thank the Springer editors Claus Ascheron and Angela Lahee for their patience during the preparation of the manuscript.

Augustusburg,
June 2002

Andreas Heilmann

Contents

1. Introduction

Composite materials, that is, materials that develop by mixing two or more basic constituents, are a topic of materials science with dramatically increasing interest [1–4]. Applications of fiber composite materials in particular have increased enormously as a result of their mechanical properties. Apart from these materials, applications of nanostructured composite materials, in which one or both of the basic components are structured in the nanometer region, are still in their early stages.

Amongst these nanostructured materials, insulating materials with embedded metal nanoparticles are under focus because of their special structural properties and the extraordinary optical and electrical properties that these confer upon them [5–7]. The nanostructure of such composite materials is determined by the spatial distribution, size and shape of the dispersed metal particles and also by the material properties of the basic constituents themselves. Knowledge of the nanostructure is the key to understanding their macroscopic optical, electrical and mechanical properties.

Beside the relationships between nanostructure and optical and electronic properties, very small metal particles dispersed in an insulating matrix exhibit exceptionally interesting physical properties due to quantum size effects [8–12]. Further, effects are possible for metal particles such as a decrease in melting point [13] or superconductivity although the *bulk* metal does not convert into the superconductive state as at Bi particles [14].

Amongst the wide range of insulating materials with embedded metal nanoparticles, thick or thin insulating layers with embedded nanoparticles have raised special interest. Examples are cermet films (ceramic–metal composite films) or thin polymer films with embedded metal nanoparticles. Polymer thin films are especially suitable as host materials for nanoparticles, whilst their chemical structure and physical properties can be very different. Further, extensive management of the nanostructure is possible during the deposition process of polymer films with embedded nanoparticles. This can be done, for example, by self-organization of colloidal metal particles in polymer solutions or by combination of various vacuum deposition processes.

Up to now, most nanostructural investigations of polymer films with embedded nanoparticles have considered first and foremost only the content of metal particles in the film as a whole. This filling factor quantifies the metal content in the whole composite film and can be specified both as a mass filling factor f_M and a volume filling factor f_V. Since the densities of the metal and the insulator often differ greatly, the volume filling factor of the metal f_V (hereafter denoted f) will be used in most cases. A determination of the filling factor can be made from the simple equation

$$f = \frac{m/V - \rho_{\text{ins}}}{\rho_{\text{me}} - \rho_{\text{ins}}} ,$$

where ρ_{me} is the density of the metal and ρ_{ins} is the density of the insulator, for which the volume V of the film (sample area multiplied by film thickness) and the densities of the basic materials must be known. For example, the mass m of the film can be determined by weighing the substrate before and after film deposition.

Depending on the filling factor f, three structure ranges can be distinguished in insulator films with embedded nanoparticles:

- $f \leq f_c$ – insulating structure range,
- $f \approx f_c$ – percolation range,
- $f \geq f_c$ – metallic structure range.

If the filling factor is below the percolation threshold $f \leq f_c$, the metal particles exist separated from each other. The metal-containing film has electrically insulating properties, but the conductivity is significantly higher with embedded metal particles than the conductivity of the pure insulating material. The percolation threshold f_c is defined as the filling factor where the film switches from an insulating to a metallic conductive film. Changes in the d.c. electrical conductivity in the percolation area may amount to eight or more orders of magnitude. In the metallic structure range, particles are no longer completely separated by the insulator matrix, and so the composite film has a higher electrical conductivity, although far below bulk conductivity in a solid state metal.

So far, a uniform distribution of the metal particles in the insulator matrix has been assumed. This becomes less probable as layers become thinner. During film deposition, a laterally and vertically inhomogeneous nanoparticle distribution often develops. It can be observed that to differing degrees the particle distribution does not form in the same way on the interfaces with the substrate and within the film. The actual nanostructure of a real metal-particle-containing insulating film is very complicated and varied, depending on the fabrication parameters and the different possibilities for particle generation.

In the following, this will be discussed by means of examples for the embedding of metal particles into an insulating matrix (Fig. 1.1). A distinction must first be made between lateral and vertical particle distribution. As the film thickness decreases, the ideal case of a laterally and vertically homogeneous nanostructure becomes less probable.

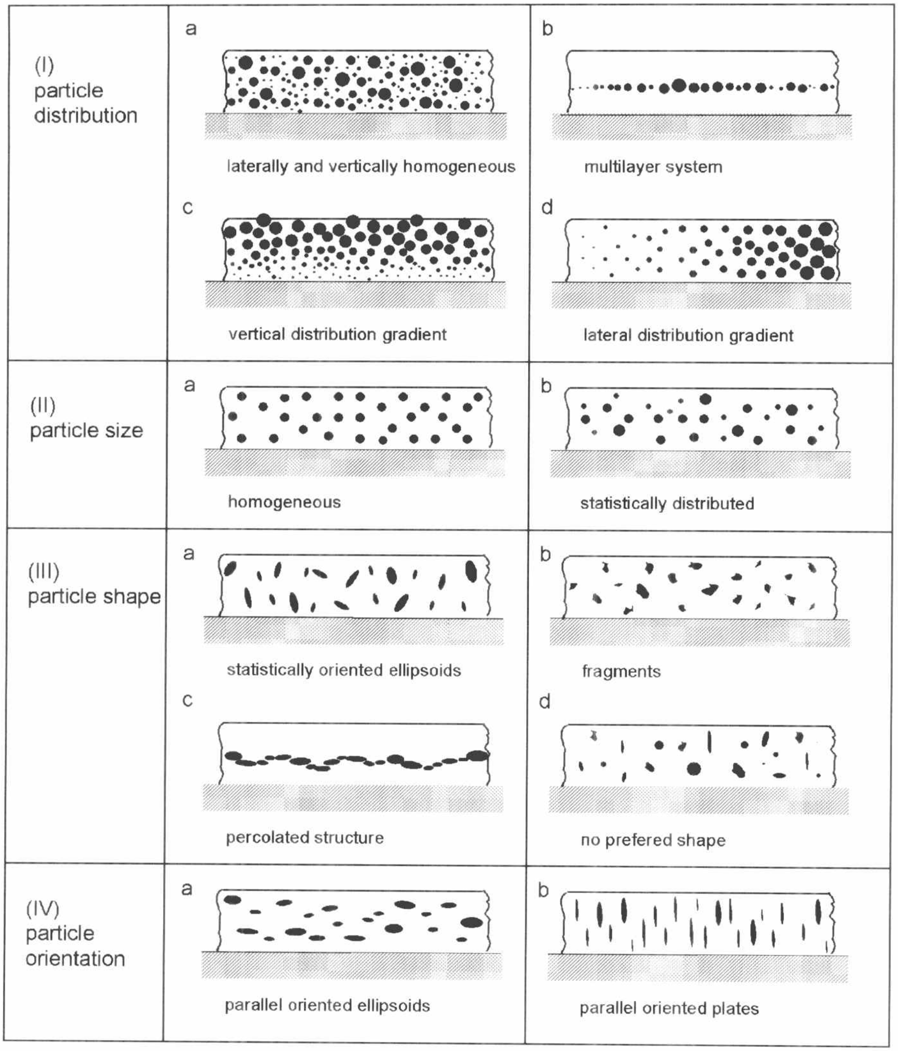

Fig. 1.1. Distributions of particles embedded in another medium

Laterally homogeneous films are often found in which metal particles are practically embedded in one plane, and not on top of each other. In this case it makes sense to call it a multilayer system consisting of a first polymer layer, a polymer layer with embedded metal nanoparticles and a second polymer layer. The filling factor should be used only for the metal-containing layer, considering that the optical properties are determined only by the size and number of the embedded particles and not by the thickness of the embedding, a mostly transparent polymer matrix.

A vertical distribution gradient of the metal particles can be generated by an appropriate choice of fabrication conditions. This film nanostructure is used, for example, for the metalization of polymeric materials in order to resolve the large macroscopic interface between metal and polymer into many small microscopic interfaces, and thereby increase the adhesive strength of the subsequently deposited metal film. Here, a determination of the filling factor is only possible for the whole film and is not actually meaningful.

Metal-containing polymer films with a lateral particle distribution gradient have a continuously changing metal content over a larger substrate area. Therefore, the size and shape of the embedded metal particles change as the metal content increases. Experimentally determined filling factors can only give an average value for a defined area of the film. Metal-containing polymer films with a continuously changing metal content represent an ideal subject of investigation when determining the influence of different particle sizes and shapes on the optical and electrical properties of composite films.

Apart from the spatial distribution of the metal particles in the polymer film, particle size is also an important parameter. Particles can possess either an almost uniform size or else be subjected to a statistical size distribution. For the investigation in particular of the collective optical properties of the metal particles, a uniform particle size is often demanded, but is seldom realized experimentally.

Furthermore, the shape of the particles greatly influences physical properties. So far, only spherical particles have been studied. However, particles must also be considered that do not bear the slightest resemblance to a sphere. Particles with the shape of rotationally symmetric ellipsoids can be embedded, as can non-rotationally symmetric, fragment-like particles. For ellipsoidal particles, the ratio between major and minor axes can be constant or subject to statistical distribution. In addition, the different orientations of the ellipsoids with respect to the substrate must be considered. A preferred direction may or may not exist. This is very important for the physical properties of films with very long elongated spheroidal particles.

The complexity involved in describing nanostructures is demonstrated by comparing various percolation structures (Fig. 1.1 IIIc) with those formed by parallel oriented ellipsoids (Fig. 1.1 IVa). Both films have the same filling factor in relation to the total film thickness, but a different vertical particle distribution. This leads to few differences in the optical properties, but very different electrical transport properties. There are only small spacings between the particles and a percolation structure with the formation of conducting paths can be observed in Fig. 1.1 IIIc. The electrical d.c. conductivity is much higher for a film with this percolation structure than for a film without it.

Depending on the various types of metal embedding that have been discussed, it can be seen that the filling factor f is only meaningfully applicable to describe the nanostructure if polymer films with embedded metal nanoparticles have a homogeneous lateral and vertical particle distribution. For all other nanostructures, the filling factor seems to be rather irrelevant, and a simple determination of the filling factor with the weighing method described previously does not yield any information suitable for describing relationships between nanostructure and physical properties. Extensive nanostructural analysis is needed in order to determine the lateral and vertical particle size and shape distribution.

A large number of modern analytical techniques are available for determining the nanostructure of polymer thin films with embedded nanoparticles. Transmission electron microscopy (TEM) is the most appropriate and powerful amongst these. However, it is not sufficient to carry out simple lateral investigations of the nanostructure. It is also necessary to investigate the vertical nanostructure with the help of a cross-sectional sample preparation. The differences in the nanostructure between the film with a percolation structure and that with embedded parallel oriented ellipsoids in Figs. 1.1 IIIc and IVa are only visible in the vertical view, whereas the lateral electron microscope images look almost identical. It is also useful to support TEM nanostructure investigations with at least one additional analytic method such as photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES).

Up to now, a time constant and fixed nanostructure has been assumed for the polymer film with embedded nanoparticles after it is deposited. However, possible modifications in the nanostructure must be considered, for example, due to thermal treatment. It is obvious that small changes in the particle shape and size distribution close to the percolation threshold can generate significant changes in electrical d.c. conductivity.

In contrast to ceramic or oxide thin film matrices like Al_2O_3, MgO or SiO_2, polymer matrices possess weaker thermal stability. However, modifications in the nanostructure due to laser irradiation or electron beam irradiation can be much more easily realized and offer a great variety of possibilities for position-resolved nanostructural modifications and artificial nanostructures.

When changes occur in the nanostructure, it is necessary to study the particles themselves, the interface between matrix and particle, and the atomic diffusion of the metal through the matrix. Nanostructural changes can result in shape modifications due to recrystallization or in the unification of two neighboring particles (coalescence). Single particle migration or the formation of chemically modified shells around the metal particle are also observed.

For these investigations of nanostructural changes, very thin polymer films are particularly suitable due to their transparency in TEM. For fabrication of the thin polymer matrix, a vacuum deposition technology called plasma polymerization was therefore selected.

The use of plasma polymerization for the fabrication of thin polymer films is an established, low-pollutant method which is compatible with other thin film technologies, especially in microelectronics. Consequently, this deposition method has an increasing number of applications. Metal particles are embedded during deposition of the plasma polymer film, mainly by simultaneous metal evaporation or metal sputtering. Low-thickness plasma polymer films (< 200 nm) are mainly optically transparent in the visible spectral region, and they are also transparent in TEM. Hence, films with embedded metal particles can be observed directly in TEM without further thinning. Another advantage of plasma polymer films is that their chemical structure and hence also their electrical and optical properties can be varied by changing deposition conditions.

Through combination of two vacuum deposition technologies, polymer films with embedded nanoparticles can be fabricated with a very large variety of nanostructures. This begins with laterally and vertically homogeneous metal-containing films and continues with multilayer systems and metal-containing films with lateral and vertical particle distribution gradients (see Fig. 1.1). In particular, films with a lateral particle distribution gradient enable a comprehensive correlation of nanostructure with electrical and optical properties for the different particle size and shape distributions and uniform matrix properties.

To study the relationships between nanostructure and nanostructural changes on the one hand and optical and electrical properties on the other, this book focuses on plasma polymer thin films which are an ideal matrix for embedded nanoparticles. Investigations concentrate on metal nanoparticles of silver, gold and indium. The optical properties of silver and gold particles are especially interesting because the plasma resonance absorption in the visible region depends strongly on particle size and shape distribution. Indium particles have been selected because they present a large number of possibilities for generating nanostructural changes.

Because of the very complex interface properties of metal nanoparticles in self-organized nanoparticle assemblies and also in order to focus discussions of the nanostructure–property relationship, self-organized nanoparticles embedded in polymer matrices will be considered for comparison. Self-organized polymer films containing metal nanoparticles, as well as the chemical properties of metal clusters are reviewed in [15–18], for example.

The book is organized as follows. Film fabrication is described in Chap. 2, where emphasis is placed on characterising the plasma polymer matrix material. The fabrication of plasma polymer thin films with embedded metal nanoparticles by metal sputtering or by metal evaporation during plasma polymerization is explained in detail.

Chapter 3 describes characterization of the nanostructure of plasma polymer films with embedded metal nanoparticles using transmission electron microscopy and photoelectron spectroscopy. Here the main point is to determine particle size and shape distributions in the lateral and vertical directions.

According to the description of possible physical processes that lead to changes in the nanostructure, the results of nanostructural changes in plasma polymer multilayers with embedded nanoparticles caused by thermal treatment, laser irradiation and electron irradiation are given in Chap. 4. Nanostructural modifications which are spatially resolved to the order of magnitude of the embedded metal particles are discussed, especially those studied through in situ observations.

In Chap. 5, the electrical d.c. conductivity of plasma polymer thin films with embedded nanoparticles is discussed. Chapter 6 gives a comprehensive description of experimental optical properties in the UV–visible–NIR spectral region for films before and after nanostructural changes. Optical properties calculated using optical scattering theories and various effective medium theories are presented.

2. Film Deposition

2.1 Plasma Polymer Thin Films

2.1.1 Organic Thin Films

The large number of applications of thin films based on polymerized hydrocarbons has led to many methods for producing this kind of film. These deposition technologies can be classified in different ways:

- By using the physical state of the starting material:
  - solid state → gaseous state → film,
  - solution → film,
  - gaseous state → film.
- By characterizing the environment during deposition:
  - ultra high vacuum,
  - pre-vacuum,
  - atmospheric pressure.
- By using the movement of the substrate during deposition:
  - dip coating,
  - spin coating,
  - roll deposition,
  - stationary substrate.
- By the film forming process which is the most common method for deposition processes starting from the gaseous state:
  - Chemical vapor deposition (CVD):
    - plasma assisted CVD (PACVD),
    - laser assisted CVD (LACVD),
    - photochemical vapor deposition.
  - Physical vapor deposition(PVD):
    - evaporation,
    - sputtering,
    - cluster beam deposition.

Further classifications are possible, for example, using the polymerization temperature, the polymerization method, or the polymerization product. These different conditions of fabrication yield thin polymer films with widely ranging properties such as:

adhesive strength: perfect adhesion properties ↔ negligible adhesion,
surface tension: hydrophobic ↔ hydrophilic,
electrical conductivity: highly insulating ↔ semiconducting (conducting),
optical behavior: transparent ↔ almost completely absorbing.

Plasma polymerization is a method for plasma assisted chemical vapor deposition of a gaseous basic material (monomer) which is polymerized during deposition. The thin polymer film grows with the assistance of an electrical gas discharge. The layer-forming process usually takes place in vacuum at a total pressure in the range 10^{-1}–10^{3} Pa and at temperatures between 290 K and 370 K. Apart from the need to clean a stationary or moving substrate, special preparations are not required.

In principle, so-called amorphous hydrogenated carbon (a-C:H) films or amorphous silicon hydrocarbon (a-C,Si:H) films can be deposited in the same way, but the energy impact for the deposition process is much higher. The transition between plasma polymer films and a-C:H or a-C,Si:H films is gradual [19], but the deposition of a-C:H films usually aims to give films with high hardness (hard coatings) or wear resistance. In the following, the films described are designed as plasma polymers but some of their properties, like adhesion, are similar to those of a-C:H films. The deposition of a-C:H and also a-C,Si:H films is described in e.g. [20–22].

2.1.2 Plasma Polymerization

The aim in the following brief commentary on plasma polymerization will be to understand the basic physical properties of films deposited in this way. Comprehensive reviews of plasma polymerisation, plasma surface treatment and plasma deposition are given in the books by Yasuda [23], d'Agostino [24], Inagaki [25] and review articles [26, 27]. The concepts underlying the gaseous state processes are extensively described in [28–30] among others.

As a method for fabricating thin polymer coatings, plasma polymerization can generally be considered as polymerization of an ionized monomer in a gaseous state by collisions with accelerated electrons in the plasma caused by an electrical discharge. The fundamental components of a reactor for plasma polymerization are a vacuum system, a plasma generator, a controllable gas inlet, and a system for in situ analysis, e.g., thickness monitoring or optical emission spectroscopy.

Because the electrical discharge usually takes place in vacuum at pressures of 1–100 Pa, the reactor (glass, quartz, high-grade steel) is evacuated by mechanical vacuum pumps, but sometimes also by additional turbo molecular pumps. In principle, plasma polymerization is also possible under normal atmospheric pressure conditions (see [31]).

Inside or outside the reactor, the gaseous or liquid monomer is often mixed with a predetermined amount of an inert gas such as argon. In a