第 13 卷　第 4 期
2005 年 8 月

光学 精密工程
Optics and Precision Engineering

Vol. 13　No. 4
Aug. 2005

Article ID　1004-924X(2005)04-0389-08

Optical coatings: trends and challenges

Norbert Kaiser, Torsten Feigl, Olaf Stenzel, Ulrike Schulz, Ming-hong Yang

(*Fraunhofer Institut für Angewandte Optik und Feinmechanik*, *Albert-Einstein-Str*. 7,*D*-07745 *Jena*, *Germany*)

Abstract: New applications in optoelectronics, photonics, telecommunication, displays, optical data processing, biomedicine, sensors, energy control, automobile, aerospace, and architecture stimulation are important developments in physics and technology of optical coatings. This paper will focus on the latest advances in the areas of new optical film systems and devices, new optical coating materials and film fabrication techniques, process control and monitoring, and different advanced applications. Particularly, focus is on optical films that combine optical design with microstructural features tailored on the nanometer and micrometer scales. Evaluation of film stability and integrity in harsh industrial environments and their compatibility with organic polymers are important as well.

Key words: optical coating; layer concept; nano-structure; multilayer optics; overview

1　Introduction

Today, optical coating has been regarded as one of the most important segment in optics technology[1]. It can sufficiently improve the performance of the whole optical system, satisfy the function requirements, and therefore is an intensively active research field worldwide.

Optical coatings can be found in nearly every technical application starting with telecommunications, space technologies, and lasers. Meanwhile, it plays a significant role in many fields development, such as physics, chemistry and synchrotron emission application. The efficiency of numerous applications and products in innovative and future technology fields is still limited by the quality of optical coatings. All optical coatings rely on control of nanodimensions. Thus, optical coatings are considered as one of the major enabling technologies for further progresses in many innovative applications and future developments.

2　Innovative layer concepts

Current research interests focus on the development of optical coatings with extraordinary optical and non-optical properties. Emphasis is made on the application of plasma-ion assisted electron beam evaporation techniques for oxide materials, in combination with optical broadband in-situ monitoring[2]. Despite of rather traditional all dielectric as well as metal-containing interference coatings, progress is going on in the fields of rugate filters, resonant grating waveguide structures, and plasmon-boosted interference coatings[3].

2.1　Rugate filters

An optical coating with a sinusoidal refractive index profile is called a rugate filter. These filters are candidate systems for high performance notch filters. The required smooth refractive index profile may be achieved in terms of a mixture of a high index and a low index layer

---

Received date: 2005-06-06; **Revised date**: 2005-06-16.

materials with a smoothly varying mixing ratio.

Fig. 1 shows a cross sectional image of the first two periods of a rugate filter built from a mixture of silica and niobia. The concentration (and refractive index) profile is visualized through the bright to dark contrast in the image. Obviously, there is a smooth refractive index profile, which is in fact already close to the intended sinusoidal one (white line).

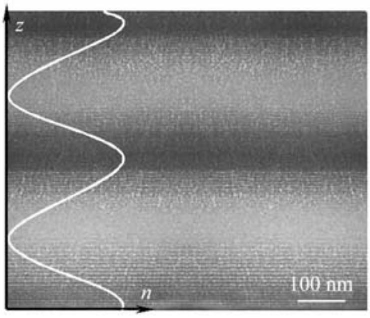


Fig. 1 TEM-cross section of a rugate filter

Fig. 2 sketches the normal incidence reflectance of such a rugate filter built from 20 periods designed to a rejection central wavelength of 1 064 nm. For the sake of comparison, the figure also shows the reflectance of a quarterwave stack built from pure silica and niobia.

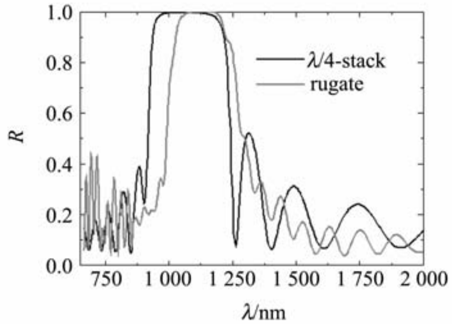


Fig. 2 Measured reflectance of a rugate filter and a quarterwave stack

2.2 Plasmon boosted interference coatings

Plasmon boosted interference coatings represent a new type of spectrally selective light absorbers. They are essentially a synthesis from a classical interference coating and a highly absorptive noble metal island film. The excitation of surface plasmons in the metal islands offers an effective absorption mechanism, while the main absorption line characteristics (frequency and oscillator strength of the absorption structure) may be controlled by experimental preparation parameters of the metal island film.

The general idea of this approach is to combine the intrinsic flexibility of optical properties of noble metal island films with the filtering properties of optical interference coatings. The first experimental results obtained from silver-based systems are promising (Figs. 3 and 4).

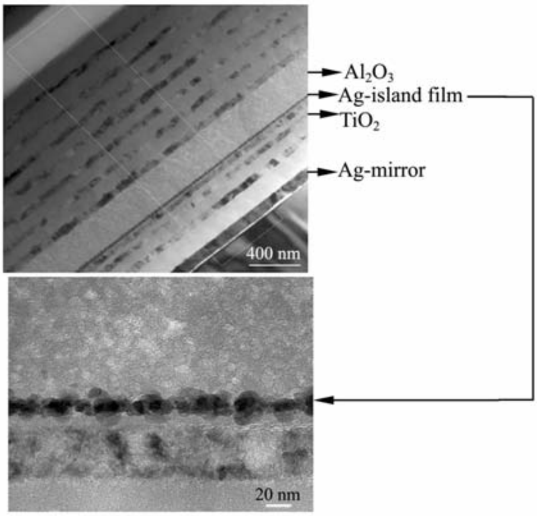


Fig. 3 Interference coating with incorporated silver island film (plasmon boosted coating) in TEM crosses section.

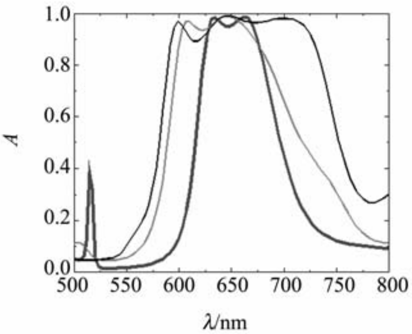
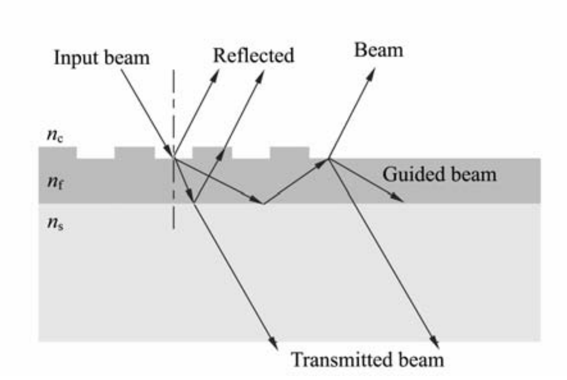


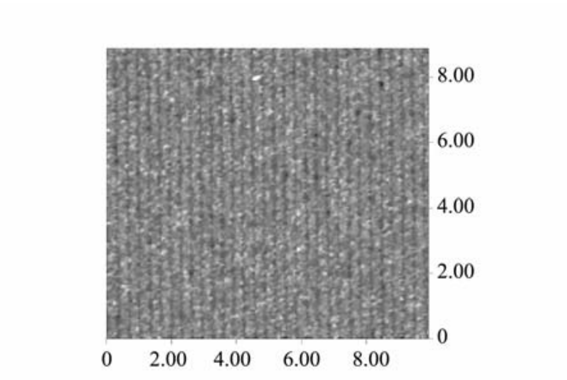
Fig. 4 Measured absorption spectra of plasmon boosted coatings based on silver island films

2.3 Resonant grating-waveguide-structures (GWS)

Extremely narrow line reflectors may be designed on the basis of GWS. Instead of a vertical stack of dielectric films, in a GWS we have a laterally periodic structure. Fig. 5 (a) shows the principal scheme of a GWS. In resonance conditions, the transmitted light is completely suppressed, theoretically leading to 100% reflection in the case that losses are negligible.



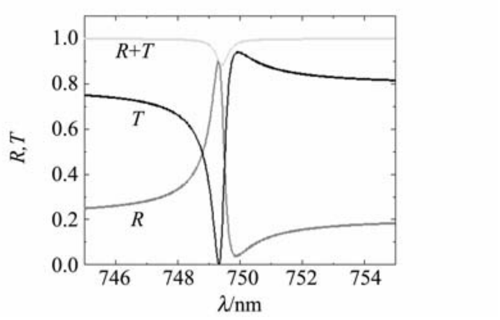
(a)



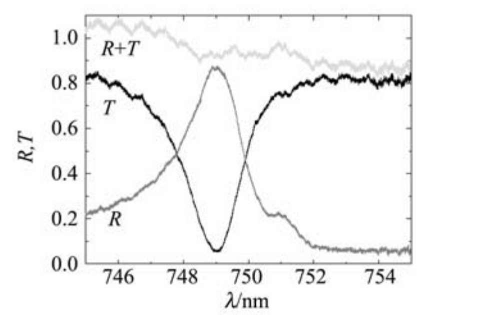
(b)

Fig. 5 (a) Scheme of a GWS; (b) AFM-image of a GWS surface with titania as top layer

GWS are promising candidates for narrow line reflectors with a rejection bandwidth down to the subnanometer region. Fig. 6 shows simulated (a) and measured (b) spectra of a GWS. The structure consists of a patterned fused silica substrate with a grating period of 330 nm, overcoated with a titania film[4] (also compare Fig. 5 (b)).



(a)



(b)

Fig. 6 (a) Calculated reflectance (R) and transmittance (T) for a GWS (TE wave at 10° incidence angle); (b) experimental spectra

3 Coating and nano-structuring on plastics

Injection moulded or hot-embossed polymer optics will replace glass optics as long as improved properties or lower costs can be achieved with the plastic parts. Highly transparent thermoplastic polymers offer significant weight reduction, cost saving and manufacturing advantages for optical components (Fig. 7). Besides several well-known types of poly-methylmethacrylat (PMMA) and poly-bisphenol-a-carbonat high transparent cycloolefin- polymers and -copolymers enter the optical applications. For plastic optics there are two main challenges for coating, the first being the same as that already known from glass optics[5]. Optical interference coatings are required to provide a specific optical function within a desired spectral range. The most common applications are antireflection

(AR) coatings to increase the transmitted light. Other important optical coatings established on glass optics are filters for defined wavelength ranges, beam splitter and metallic or dielectric mirrors.

Vacuum deposition of optical coatings at low substrate temperature is realizable with Plasma Ion Assisted Deposition- technology (Plasma-IAD) using Leybold APS 904. A thermally evaporated film is bombarded during its growth with energetic ions emitted by the Advanced Plasma Source (APS). Applying Plasma-IAD on plastics, the low-pressure plasma can be used in manifold way to modify the polymer surface properties as well as to adjust the mechanical stress of inorganic thin films.

Fig. 7 Coated plastics

Coating on plastics requires substrate specific vacuum processes. The suitability of the miscellaneous thermoplastic polymers for vacuum coating processes must be evaluated with respect to the degree of damage these substrates will sustain when in contact with plasma and high-energy radiation. Satisfactory layer adhesion on all plastic substrates exhibits boat-evaporated oxide layers, which can be deposited without the influence of radiation or plasma emissions. Hence, those layers grow on unheated polymer substrate with very low density and show bad mechanical properties therefore. Electron beam gun evaporated oxide layers deposited with plasma ion assistance show the best adhesion on certain types of polycycloolefines[6]. These materials meet the requirements for the deposition of very thick interference coatings like scratch resistant antireflective coatings.

The problems with handling polymers in coating processes stimulate researcher and manufacturer to look for new coating designs or for alternative coating or treatment techniques. One examples of this development is the design concept AR-hard for antireflection purposes[7]. The AR-hard coating is scratch resistant itself because of its high overall thickness. Antireflection coatings of the AR-hard type can be understood as an arrangement of symmetrical three-layer periods, each of them consisting of a very thin high refractive index layer H in the middle of two thick low refractive index layers L (Fig. 8). Typical layer materials are SiO_2 as a hard oxide with low refractive index and TiO_2 as a high refractive index material. The low amount of high-index material inside coatings of type AR-hard can be an advantage for cold deposition processes.

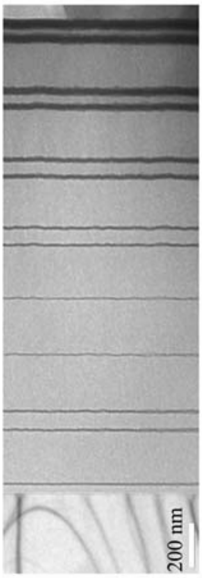


Fig. 8 Transmission electron micrograph of coating AR-hard deposited on silicon substrate

An alternative possibility to decrease the reflection on polymer surfaces is the use of appropriate layers with decreasing effective index from substrate site to air. Our investigations show that the application of special ion bombardment conditions leads to stochastic antireflective structures on acrylic surfaces, so-called "NANO-moth eyes". The plasma source of Leybold box-coater APS904 was used to perform the etching step. The ion energy, the treatment time and the gas composition determine essentially the modification of topography as well as the optical properties. The combination of argon and oxygen in the plasma for a treatment time of several hundred seconds leads to excellent antireflective properties on PMMA surfaces[8]. From a first very fine-grained structure, larger agglomerates are formed with increasing treatment time. These features are almost uniform in size and are stochastically distributed over the surface (Fig. 9).

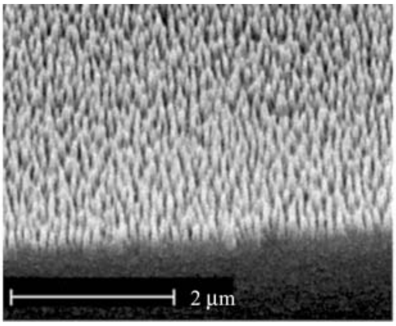


Fig. 9 Scanning electron micrograph of a "NANO-motheye"-structure on PMMA

By applying the plasma treatment to both sides of a PMMA sheet, the average reflection can be decreased to less than 1% in a wavelength range from 400 nm to 1000 nm. The performance of the antireflective structure is much less sensitive to the angle of light incidence than interference coatings. In summary, this procedure should be favorably applied on curved and structured surfaces but only on surfaces that do not have to be touched or cleaned later. Cost effective mass production may be possible by direct ion etching for small optical parts as well as by replication of the structure onto bigger parts.

4 EUV and soft X-ray multilayer optics

The accurate deposition of high reflective and laterally graded multilayers on ultra precisely polished substrates is one of the major challenges of EUV optics development today. According to the PO box requirements of an extreme ultraviolet lithography tool, EUVL at 13.5 nm can be regarded as the technology driver to develop multilayer coated optical components for the EUV spectral range and the soft X-rays. To meet the multilayer coating requirements, a New EUV Sputtering System-NESSY has been developed (Fig. 10).

Fig. 10 DC magnetron sputtering system NESSY

4.1 Conception

The deposition of EUV substrates is realized by DC magnetron sputtering. The fast spinning substrates move on a circular path underneath the sputter sources (sputter down). The system is equipped with four rectangular magnetrons, 600 mm × 125 mm each. Hence, up to four different materials can be deposited during one rotation of the substrate (e.g. molybdenum and silicon and two different interdiffusion layer materials). The layer thickness can be adjusted in the sub Angström range by the rotation speed and the power of the corresponding sputter source. The simultaneous coating of two ϕ450 mm substrates or three ϕ300 mm substrates is realizable. Substrates are transferred via load lock from the clean room area into the sputtering chamber (Fig. 11).

Fig. 11 Substrate load lock

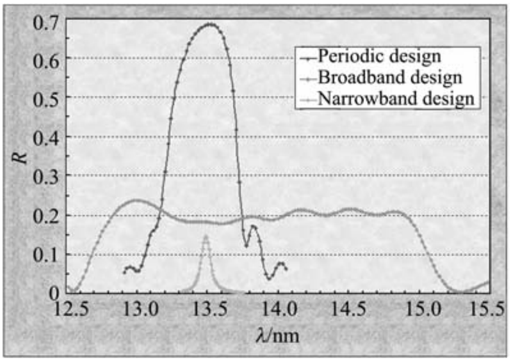
To optimize the lateral thickness homogeneity the substrates are spun up to 500 r/min during the deposition process. The target-substrate-distance is variable allowing the installation of shutters to deposit laterally graded multilayers. Special effort has been made to construct the cathodes. Different configurations of the magnets have been successfully realized in order to assure the highest flexibility for different coating materials in terms of homogeneity requirements and adatom energy. All magnetrons work stable at a working pressure of less than 5×10^{-1} Pa in argon atmosphere. The specifications are summarized in Tab. 1:

Tab. 1 NESSY-specifications

Substrate size	up to ϕ300 mm
Substrate stations	3 stations for ϕ300 mm
Sputter sources	4 magnetrons, 600 mm×125 mm
Thickness homogeneity	±0. 1% on 150 mm, ±0. 2% on 300 mm
Sputter distance	variable
Substrate rotation	≤2 r/min
Base pressure	$<8\times10^{-7}$ Pa

4. 2 Mo/Si multilayer mirrors

Mo/Si multilayers with different film designs were realized. Beside the maximization of the peak reflectivity using a periodic multilayer design, the maximization and minimization of the FWHM were designed and realized using special broadband and narrowband multilayer designs[9]. , respectively. Normal incidence reflection measurements were performed with synchrotron radiation at the PTB Berlin (BESSY II), Germany. Fig. 12 compares the measured reflectance of Mo/Si multilayer mirrors with a periodic, a broadband and a narrowband design.



$R=68.8\%$ $\lambda=13.5$ nm FWHM = 0. 50 nm
$N=60$; $R\approx20\%$ $\lambda=13\sim15$ nm FWHM=2. 33 nm
$N=60$; $R\approx14.6\%$ $\lambda=13.5$ nm FWHM=0. 077 nm
$N=40$

Fig. 12 Measured EUV reflectance of Mo/Si multilayers

The lateral layer thickness distribution was optimized with specially formed masks fixed close to the cathodes. Homogeneity of ±0. 1 % on 150 mm and ±0. 2 % on 300 mm has been demonstrated with Mo/Si multilayers 10.

4. 3 High-temperature $MoSi_2$/Si and Mo/C/Si/C multilayer coatings

The application of multilayer optics in EUV Lithography requires not only the highest possible normal-incidence reflectivity but also a long-term thermal and radiation stability at operating temperatures. This requirement is most important in the case of the collector mirror of the illumination system close to the EUV source where a short-time decrease in reflectivity is most likely. A serious problem of Mo/Si multilayers is the instability of reflectivity and peak wavelength under high heat load. The instability of Mo/Si multilayers becomes especially critical at elevated temperatures of more than 200 ℃, thus limiting the possible applications of Mo/Si multilayers for coating of the EUVL collector mirror.

The development of high-temperature multilayers was focused on two alternative Si-based systems: $MoSi_2$/Si and Mo/C/Si/C multilayer mirrors. The multilayer designs as well as the deposition parameters of both systems were optimized in terms of high peak reflectivity at a wavelength close to 13.5 nm and a working temperature of 400 ℃. Annealing was carried out under vacuum at elevated temperatures of up to 500 ℃ for up to 100 h.

Small thermally induced changes of the $MoSi_2$/Si multilayer properties were found but they were independent of the annealing time at all temperatures examined (Fig. 13). A wavelength shift of −1.7 % and a reflectivity drop of 1.0 % have been found after annealing at 500 ℃ for 100 h. The degradation of optical properties can be explained by crystallization processes of $MoSi_2$ layers (Fig. 14)[11].

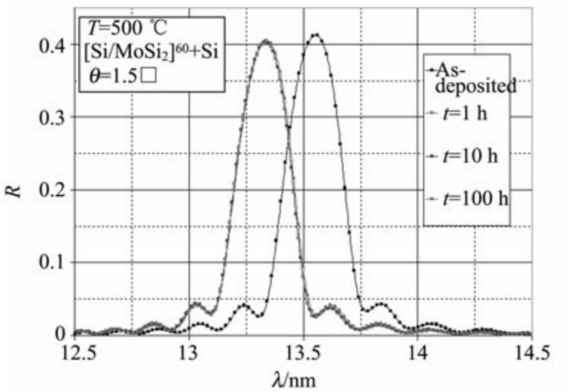


Fig. 13 Measured $MoSi_2$/Si reflectivity, annealing at 500 ℃ for 1, 10 and 100 h.

The optical properties of Mo/C/Si/C did not change for temperatures of up to 300 ℃. A wavelength shift of −2.1 % and a reflectivity drop of 1.5 % were found after annealing at 500 ℃ for 100 h. For temperatures above 400 ℃ a time-dependent degradation of the optical properties can be observed (Fig. 15).

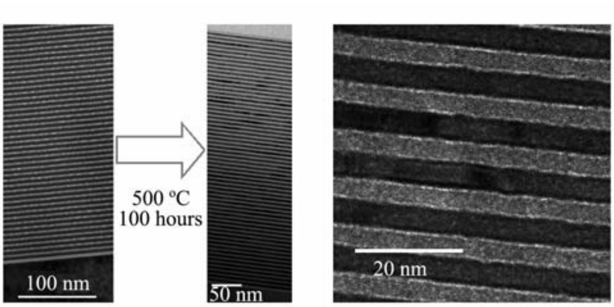


Fig. 14 TEM of $MoSi_2$/Si, As-deposited TEM and HR TEM of $MoSi_2$/Si after 500 ℃/ 100 h annealing; XRD analysis of structure: crystallization of $MoSi_2$ at 500 ℃

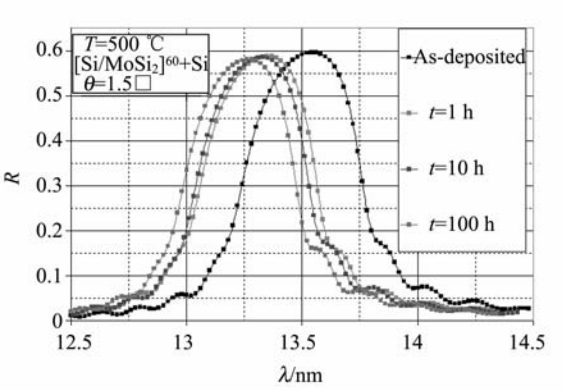


Fig. 15 Measured Mo/C/Si/C reflectivity, annealing at 500 ℃ for 1, 10 and 100 h.

The combination of high thermal stability and good optical properties of $MoSi_2$/Si and Mo/C/Si/C multilayer mirrors underlines their potential for use in the coating of EUVL collector optics.

5 Outlook

In the course of the rapid development of the optical technologies, the optics communities will be challenged by new demanding requirements revolutionising the present production cycles for optical coatings and components. As major pace makers, information technology, space technology, medicine, new laser applications and life sciences are driving optical thin film technology forward to new frontiers, which are far beyond the present capabilities of established deposition processes and production strategies.

In order to master these complex tasks of optical technologies, the experience and the infrastructures of the coating producers and the research institutes have to be combined. Only on the basis of an interdisciplinary, joint research programme and open communications and exchanges involving partners from the world wide, the critical concentration of expertise can be reached, to develop the high quality optical coatings demanded in the near future. Nowadays, optical coatings research clusters in Germany and China have grown up with their own remarkable characters in the world, the intercommunication between these clusters is necessary and of great interest to both sides.

6 Acknowledgements

High resolution TEM analysis of the samples has been performed by the group of Ute Kaiser, University of Ulm.

References:

[1] Norbert Kaiser, Hans K. Pulker (Eds.). Optical interference coatings[J]. *Springer Series in Optical Sciences*, 2003,88:

[2] S. Wilbrandt, R. Leitel, D. Gäbler, O. Stenzel, N. Kaiser. In-situ broadband monitoring and characterization of optical coatings postervortrag auf der[C]. *OIC* 2004, *in Technical Digest*, 2004.

[3] O. Stenzel. New challenges in optical coating design[C]. *Advances in Solid State Physics*, 2003:875-888. *Springer-Verlag Berlin Heidelberg* 2003.

[4] O. Stenzel. The physics of thin film optical spectra: an introduction[C]. *Springer Series in Surface Sience*, *Springer Verlag Berlin*, 2005.

[5] U. Schulz. *Coating on plastics, in s. bäumer (Ed.): handbook of plastic optics[M]*. Wiley-VCH (2005), ISBN: 3527404244.

[6] P. Munzert, U. Schulz, N. Kaiser. Transparent thermoplastic polymers in plasma-assisted coating processes[J]. *Surf. Coat. Technol.*, 2003,173-174, 1048-1052.

[7] U. Schulz, U. B. Schallenberg, N. Kaiser. Symmetrical periods in antireflective coatings for plastic optics[J]. *Appl. Opt.*, 2003,42:1346-1351.

[8] A. Kaless, U. Schulz, P. Munzert, N. Kaiser. *NANO-motheye antireflection pattern by plasma treatment of polymers*[M]. Surf. Coat. Technol, 2005. (in press, online available at www. sciencedirect. com)

[9] N. Kaiser, S. Yulin, T. Feigl, H. Bernitzki, H. Lauth. EUV and soft X-ray multilayer optics[J]. *SPIE*, 2004, 5250:109-118.

[10] T. Feigl, S. Yulin, W. Stckl, N. Kaiser, H. Bernitzki, H. Lauth: Large area sputtering system for EUVL optics[C]. *Proc.* 2nd *International EUVL Symposium*, *Sep* 30 - *Oct* 2 2003, *Antwerp*, *Belgium*.

[11] S. Yulin, N. Benoit, T. Feigl, N. Kaiser. High-temperature $MoSi_2/Si$ and Mo/C/Si/C multilayer mirrors[C]. *Proc.* 3rd *International EUVL Symposium*, Nov 1-4, 2004, *Myiazaki*, *Japan*.

Brief professional biography of the author:

Norbert Kaiser received his Diplom Physiker in 1974, his Dr. rer. nat. in 1983 and his Dr. habil in 1999 from the University of Jena. After 9 years of resarch on nucleation and growth of thin films, he joined the Optical Thin Film Group of the Physikalisch Technisches Institut, Jena, and was responsible for R&D on coatings for the UV. Since 1992 he heads the Optical Thin Film Department and is deputy director of the Fraunhofer Institut Angewandte Optik und Feinmechanik in Jena. He has authored a large unmber of papers and patents on nucleation, growth, and structure-related properties of thin optical films. He is editor of "Optical Interference Coatings" in Springer Series in Optical Sciences (2003), president of technical committee "Thin Films for Optics and Optoelectronics" of the European Society of Thin Films and chair of Numerous International Conferences.