A journey from ancient China: bronze mirrors to picometer-shaped interference coatings

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The basic form of a mirror as a cast metal object, with a highly polished reflective surface and relief decorations at the back, has remained unchanged throughout most of China's history. The earliest known Chinese mirrors date back to approximately 2000 BC. For almost a hundred years, advancements in the broad area of optical coatings have been used to shape mirror reflectivity in an inconceivable manner. For example, mirrors for deep ultraviolet (193 nm) and extreme ultraviolet (13.5 nm) are considered, playing a positive effect in lithography. Substantial improvements are expected in the efficiency of layer systems with regard to both optical performance and overall stability.

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The earliest known Chinese mirrors date back to approximately 2000 BC[1] and were produced until the late Qing Dynasty (1644–1912). The basic form of mirrors as cast metal objects, with highly polished reflective surface and relief decorations at the back, have remained unchanged throughout the approximately 4000 years of bronze mirror history in China[2]. It was during the Han Dynasty (202 BC–220 AD) that mirrors started to be mass-produced. The most popular mass-produced daily mirror was the TLV mirror, which was called as such because of the engraved symbols resembling the letters T, L, and V (Fig. 1).

Bronze mirrors gradually lost their popularity and ceased to be produced after the arrival of thin-film mirrors during the Ming (1368–1644) and Qing (1644–1912) dynasties. Instead of using solid metals, thin-film mirrors were manufactured by applying reflective metal coatings to the glass, primarily to protect the glass from corrosion and damage. The method of making mirrors out of ordinary glass was used by 16th century Venetian glassmakers in the island of Murano, where they covered rear side of plate glass with tin-mercury amalgam to obtain near-perfect reflection and imaging qualities.

Nowadays, in precision optics, the mirror substrate is shaped and polished with subwavelength accuracy before it is coated, by evaporation or sputtering, with metal and then completed by a series of protection and enhancement coatings. Around the 1940s, mirrors have also been produced with transparent coatings using the process of constructive interference. Such dielectric mirrors consist of alternating high- and low-index quarterwave layers. Within a limited spectral range, dielectric mirrors provide very high reflectance (above 99%). These are even considered indispensable in the field of laser radiation. In modern optics, mirrors are one of the major focuses of study on thin-film coating.

Polished metal surfaces are highly reflective. Accordingly, thin metal coats on smooth substrates like simple glass will make excellent mirrors. Strong optical properties of metals (e.g., Al, Ag, and Au) are determined by the presence of free electrons. Figure 2 shows the spectral reflectance of Al, Ag, and Au.

Metallic coatings are reflective in a broad spectral band and over a broad range of angles of incidence. Nonreflected radiation is absorbed and converted into heat. Suitable metals include gold (Au) for infrared, silver (Ag) for visibility (VIS), and aluminum (Al) for ultraviolet (UV) radiation. Highly reflective ($R \sim 90\%$) metals, such as Al, Au, and Ag, if used for first-surface mirrors, require protective layers against mechanical and chemical damage. Since Ag is particularly sensitive and needs special protection, most VIS mirrors have Al coatings. Protective layers diminish reflection. The optical thickness of the protective layer must be either very small (a few nanometers only), or about $\lambda/2$ thick. Moreover, thick protective layers narrow down the intrinsic broadband property of the metal mirror. However, a double layer (e.g., $\lambda/4$ TiO_2/Al_2O_3) will not only protect the metal mirror but also considerably increase its reflectance within a limited spectral range. Such mirrors are referred to as enhanced metal mirrors (Fig. 3).

Hard metals, such as rhodium, nickel, and chromium, need no protection and can be used as front mirrors although their reflection is less than 70%. China's bronze mirrors were generally made of copper (Cu), tin (Sn), and lead (Rb), with about 70% Cu, 25% Sn,

Fig. 1. Bronze TLV mirror. The TLV pattern, which resembles the three Roman letters, is commonly seen at the back of bronze mirrors used during the Han dynasty (Source: http://history.chess.free.fr/images/liubo/07mirrormain.jpg).

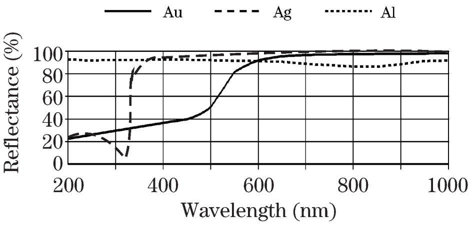

Fig. 2. Spectral reflectance of Al, Ag, and Au.

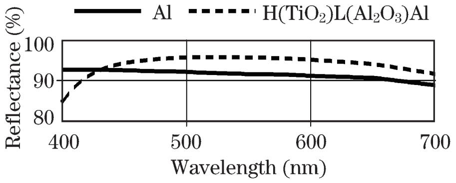

Fig. 3. Enhanced Al mirror.

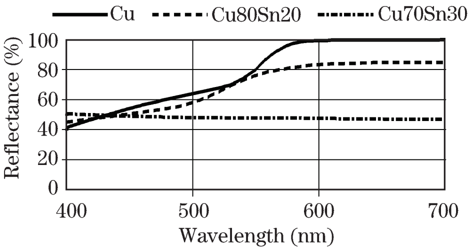

Fig. 4. Spectral reflectance for normal incidence of Cu, $Cu_{80}Sn_{20}$, and $Cu_{70}Sn_{30}$ based on complex refractive index data[4].

Fig. 5. Polymer mirror parts (Jenoptik Polymer Systems GmbH).

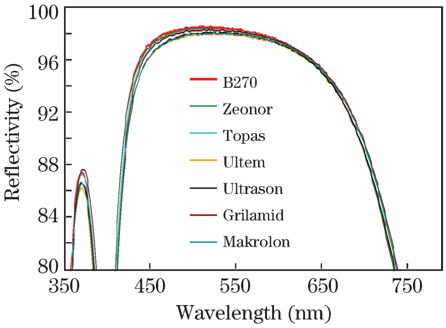

Fig. 6. Enhanced Al-mirrors on various polymers and optical glass, R (VIS) $>$ 97%.

and 5% Pb[2]; Pb facilitated grinding and polishing. The mirror's reflective surface was smoothed with scrapers and chisels, and then carefully polished with abrasives to produce highly reflective surfaces. The higher the Sn content, the more silver-like was the reflection. The color of the mirrors, however, could not be fully understood. Patrick Callet of Laboratoire Mathématiques Appliquées aux Systèmes, Ecole Centrale Paris, and Centre Français de la Couleur, investigated the visual appearance of bronze[3]. He published[4] complex indices of refraction measured by spectroscopic ellipsometry for polished surfaces of Cu, Sn, and alloys. In this study, we used this data to calculate the spectral reflectance of Cu, $Cu_{80}Sn_{20}$, and $Cu_{70}Sn_{30}$ (Fig. 4). The $Cu_{70}Sn_{30}$bronze mirrors were comparable to the original $Cu_{70}Sn_{25}Pb_5$ owing to their quite metallic appearance, neutral action over visible spectral region, and 50% reflectance and 50% absorption.

Since they are cost-effective and easy to produce, even in their complex forms, mirrors made of plastic are steadily replacing those made from glass. However, metalized polymer substrates offering highest reflectance are not yet considered state-of-the-art. Coating organic substrate materials is still a task that involves multiple problems, with insufficient adhesion of coatings on polymer substrates representing one of the main difficulties[5,6]. It has been found in experiments that Al and Ag layers showed good coating adhesion on many different polymers only if they are deposited by vacuum evaporation with certain process parameters.

High reflectance values and a good climatic stability of the metal-coated polymer parts are other important challenges to the production of plastic mirrors (Fig. 5). By performing roughness measurements on different polymer samples, and comparing reflection values obtained after coating these samples, the impact of the polymer's surface quality on the reflectance obtained by metal coating was investigated. Particularly, high reflectance values above 97% were implemented with a protected Ag mirror, as well as with dielectric-enhanced Al mirror (Fig. 6).

With these layer systems applied to several plastic substrates, excellent reflection properties were obtained, which were comparable to those in glass mirrors. Furthermore, dielectric layers used for reflection enhancement showed abilities to protect the Al coating against climatic influences.

High quantum energy and a corresponding short wavelength can give UV radiation the prominent role of providing high resolution in optics. Mainly excimer lasers have shown potential for future applications, such as in ultra-precision machining and measurement, minimal invasive brain, vascular and eye surgery, components for data communication, and large-scale integrated electronic devices. For engineers, the main challenge is to provide for efficiency. By taking advantage of the expensively generated UV photons, efficient optics, which could satisfy extreme technical demands, are required. Efficient UV optics can only be implemented by dielectric coatings. Hence, stable coatings are among the most important issues in efficiency improvement to date.

Optical lithography is the technology driver in the development of optical components and coatings for shorter wavelengths. Investigations have been concentrated on the 193 nm ArF excimer laser wavelength[7−9].

The ArF lithography technology requires minimization of optical losses resulting from scattering and absorption. Metal fluorides are common thin-film materials for 193 nm applications because of their higher band-gap energy, as compared to metal oxides. We have demonstrated that most of the common metal fluorides, such as MgF_2, AlF_3, and LaF_3[10], can be deposited by electron beam evaporation. Compared to other deposition methods, the prepared thin films obtained the lowest absorption in the vacuum ultraviolet (VUV) spectral range. Furthermore, metal fluoride thin films were prepared by plasma assistance. It has been demonstrated that they have less water content, high packing density, and low absorption in the VUV spectral range[11].

The demand to enhance optical resolution, as well as to structure and observe ever smaller details, has pushed the development of the optics field in recent years. Induced mainly by the production of more powerful electronic circuits with the aid of projection lithography, there have been increased interests in the optical components of extreme ultraviolet (EUV) spectral region[12,13]. Due to absorption, the penetration depth of EUV radiation into matter is only a few nanometers. Hence, reflective optics have to be used for imaging and light collection, such as EUV multilayer mirrors that consist mainly of alternating thin films with different refractive indices[13].

The output power of a high-power EUV source at 13.5 nm and with a 2% bandwidth, as well as the source and collector lifetime, can be counted among the major challenges of EUV lithography development to date. Current collector mirror concepts are mainly based on source geometry. Grazing-incidence Wolter collectors are commonly used for discharge-produced plasma (DPP) sources, while multilayer collector mirrors are applied to laser-produced plasma (LPP) sources. Fraunhofer IOF continues to develop different technologies for precise deposition of highly reflective and laterally graded multilayers on curved collector substrates.

Figure 7 shows a coated π source collector mirror for high-powered LPP sources; the corresponding reflectance curves can be observed in six different mirror positions. The measured peak reflectivity of the collector mirror is $R = 67.7\%$ at 13.5 nm. The ellipsoidal substrate with an outer diameter of 300 mm and lens sag of 50 mm was made of a single crystalline silicon. The Mo/Si multilayer coating was deposited by the EUV sputtering system NESSY[14].

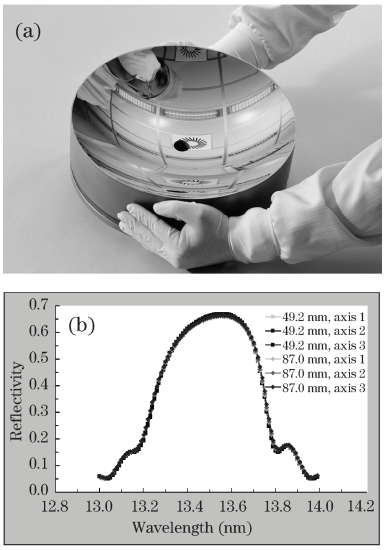

Fig. 7. (a) Mo/Si-coated EUV collector mirror for high-power LPP sources and (b) corresponding reflectance curves Measurement: Physikalisch-Technische Bundesanstalt Berlin.

Angles of incidence vary from normal incidence at the mirror center to about 22° at the mirror edge. In order to meet the Bragg condition in every position of the mirror surface, a one-dimensional lateral film thickness gradient was implemented. The deviation of 0.05 nm from the design wavelength of 13.5 nm represents the maximum period thickness error of $\Delta d/d = 0.34\%$. Thus, the absolute period thickness error that can be tolerated within the multilayer stack is $\Delta d = 0.025$ nm.

Schwarzschild objectives are increasingly used for imaging optics in the EUV spectral region because of their large aperture, high mechanical stability, and absence of chromatic aberrations. The objectives have manifold uses, from applications for EUV lithography and fundamental research using Synchrotron radiation, to imaging optics for X-ray lasers. A Schwarzschild objective consists of a convex and a concave multilayer-coated mirror. Depending on the optical path of the objective, it can be used for magnification (e.g., microscopy) or demagnification (e.g., lithography) of objects and structures. A Schwarzschild objective must meet extreme component requirements in order to implement diffraction-limited imaging at $\lambda = 13.5$ nm. The tolerable maximum surface figure error is in the sub-nanometer range. Hence, substrate surface deformation by gravitation, intrinsic mechanical stresses of the coating, and design of mechanical holder need to be taken into account-and if necessary, corrected properly. Optical components have to be positioned and centered within their low-stress mechanical holder with an accuracy of a few microns. A hydrocarbon-free mounting design is essential to minimize contamination and degradation of optical surfaces.

Apart from creating EUV Schwarzschild objectives for diffraction-limited imaging, the Fraunhofer IOF was also developed and built around various objectives for different applications in the EUV spectral range. Figure 8 shows a modified 10 × Schwarzschild objective for 13.5 nm intended to generate high focus intensities for

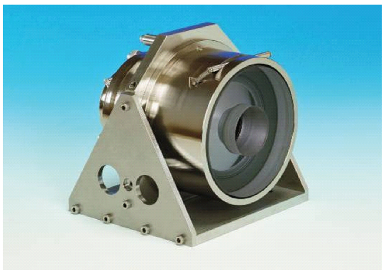

Fig. 8. 10× Schwarzschild objective for 13.5 nm. The numerical aperture of the Schwarzschild objective is 0.44. The spherical substrates are made of ULE and were coated with a high-reflective Mo/Si multilayer. A reflectivity of $R > 65\%$ at $\lambda = 13.5$ nm was measured at the clear aperture. The mechanical holder of the primary and secondary mirrors was optimized for a horizontal optical path. Both mirrors are vertically mounted using a 120° three-point support.

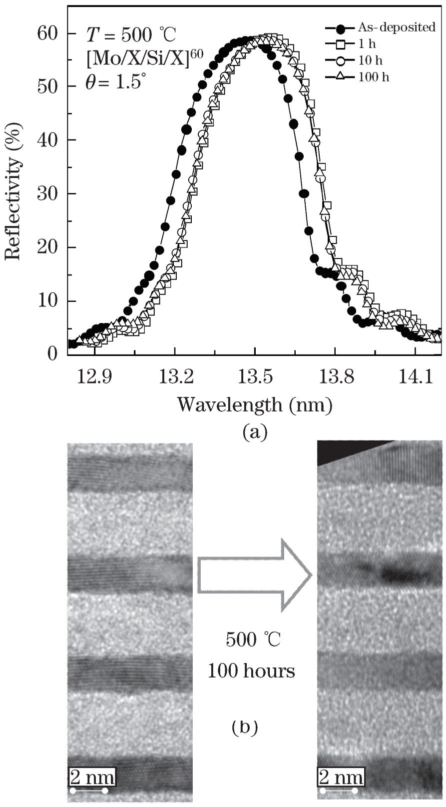

Fig. 9. (a) The evolution of the reflective properties of new interface-engineered multilayer mirrors after isothermal annealing at 500°C for 1, 10, and 100 h. (b) No change in the internal multilayer structure was found after annealing at 500 °C for 100 h.

fundamental investigations of photon-matter interactions.

Some applications of multilayer mirrors for extreme ultraviolet lithography (EUVL) require not only the highest possible peak reflectivity, but also long-term thermal stability. This requirement is particularly important for the first mirror in the illumination system, which is located closest to the EUV LPP source, especially since it is here where reflectivity decrease is most likely to happen. To combine both high normal-incidence reflectivity and superior long-term thermal stability, new interface-engineered Mo/X/Si/X multilayers (X is the material of diffusion barriers) were suggested[15]. Figure 9 shows the evolution of reflective properties of such multilayer mirrors after isothermal annealing for 100 h at a temperature of 500 °C. It can be seen that simple pre-annealing at a temperature of 500 °C for one hour can stabilize the internal structure and reflective properties of this type of interface-engineered multilayer mirror. The combination of high reflective properties and enhanced thermal stability of new interface-engineered multilayer mirrors provide good prospects for their industrial application as coatings for EUVL collector optics up to temperatures of 500 °C[16].

The lifetime of Mo/Si multilayer-coated projection optics is one of the identified issues related to the commercialization of EUVL. Water and hydrocarbons are two major contamination sources reducing the lifetime of projection optics under intensive EUV irradiation.

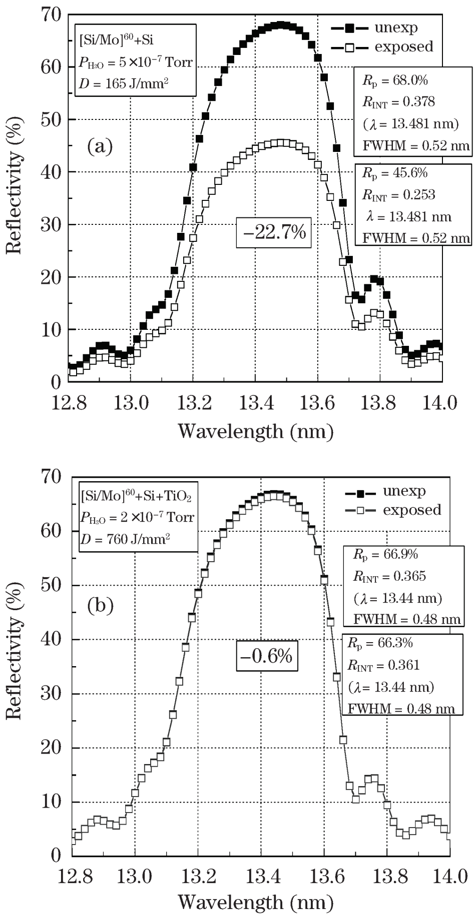

Fig. 10. Evolution of reflective properties of (a) Si- and (b) TiO$_2$- capped Mo/Si multilayer mirrors after exposure by synchrotron radiation in water vapor environment with $P = 2.7\times10^{-5}$ Pa, with EUV doses up to about 750 J/mm^2.

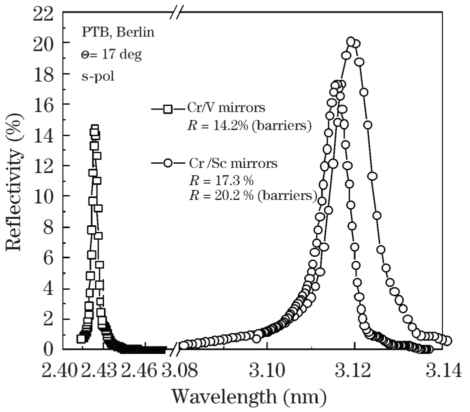

Fig. 11. Evolution of optical performance of Sc-based and V-based multilayer mirrors due to the application of diffusion barriers.

Several alternative capping layer materials, such as carbon (C), ruthenium (Ru), ruthenium dioxide (RuO$_2$), and titanium dioxide (TiO$_2$), were suggested for the protection of Mo/Si surface against oxidation. A comparative lifetime study of TiO$_2$- and Si-capped Mo/Si multilayer mirrors was performed at the NIST using a recently commissioned beamline at SURF III with an average EUV intensity of about 5.0 mW/mm^2 and a water vapor pressure of 2.7×10^{-5} Pa. The evolution of reflective properties of Si- and TiO_2-capped Mo/Si multilayer mirrors is shown in Fig. 10. The reflectivity loss of the Si-capped multilayer was 22.7%, while the reflectivity of the TiO_2-capped multilayer after thrice the exposure time dropped only by 0.6%[17].

Much effort is being offered in the implementation of high-reflectance multilayer coatings for "water window" spectral range (2.4−4.4 nm). Driving forces include prospects for high-resolution microscopy in the "water window" and for deep-space telescopes.

In recent years, new high-reflectance multilayer structures based on the scandium (Sc) and 3d-transition metals Ti and vanadium (V) have been produced for operation in the water window between carbon (λ = 4.4 nm) and oxygen (λ = 2.4 nm) K-edges. The optical performance of such mirrors is extremely sensitive to the multilayer design and interface quality (mainly, interface roughness). Until now, the maximum near-normal incidence reflectance of 17.3% at wavelength of 3.12 nm has (only) been achieved with Sc-based multilayer coatings at 400 bilayers (Fig. 11)[18]. Due to constructive interference from many interfaces, the spectral bandwidth is about 0.01 nm. To minimize interface roughness in Sc-based multilayer structures, interface-engineered designs were successfully applied. It was found that interface-engineered Sc-based mirrors with 400 bilayers have peak reflectances of 20.2% at wavelength of 3.12 nm (Fig. 11). Similar interface-engineered concepts were applied to V-based multilayer mirrors designed for wavelength of 2.42 nm, and a near-normal incidence reflectance of 14.2% was achieved (Fig. 11).

In conclusion, the first mirrors used by mankind were pools of dark, still waters. Mirrors are said to be a reflection of the soul, and this could be one reason why mirrors are considered the most important optical instrument. Consequently, the very first mass-produced optical instruments were mirrors, dating back thousands of years ago, manufactured by polishing stones or metals, and then, by "magnifying the reflection of light". This fact could explain why the practice was consistently used for many centuries. Since the skin of a solid-not the bulk-reflects the light, thin metal or dielectric coatings were identified as excellent mirrors, providing that the underlying surface is smooth, as in the case of simple transparent glass. From these mirrors, optical coatings of today are considered vital objects for research and development.

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