Thin Solid Films 532 (2013) 119–122

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Hybrid antireflective coating with plasma-etched nanostructure

Ulrike Schulz *, Peter Munzert, Friedrich Rickelt, Norbert Kaiser

Fraunhofer Institute of Applied Optics and Precision Engineering, Optical Coatings Department, Albert-Einstein-Straße 7, 07745 Jena, Germany

ARTICLE INFO

Available online 22 December 2012

Keywords:
Anti-reflection
Nanostructures
Plasma-etching
Organic layers
Physical vapor deposition

ABSTRACT

Antireflective structures with features of sub-wavelength size are appropriate as an alternative to interference coatings for obtaining antireflective properties on optical surfaces. For broadband antireflection or a wide range of incidence angles, a distinct structure depth together with a very low lateral structure size is required, which is difficult to realize. Design considerations show that also thinner nanostructured layers are useful if they are combined with compact interference layers. A nanostructured low-index melamine layer has been prepared by plasma-etching of a vacuum deposited organic thin film. In combination with homogeneous silica layers antireflection properties for a broad range of light incidence angles were achieved.

1. Introduction

Antireflective structures (ARS) have become rather well known since they were discovered on the eye of a nocturnal moth by Bernhard in 1967 [1]. The periodically structured moth eye acts as an effective antireflective medium featuring a decreasing refractive index from the substrate side to the surrounding air. Early theoretical papers approximated sub-wavelength gratings as effective thin-film stacks and used especially the effective media theory to describe its optical properties [2,3]. Sub-wavelength surface structures are typically less sensitive to the angle of incidence of light than homogeneous multilayer stacks [4,5]. A technical implementation of antireflective structures was achieved using a holographic superposition of a light-exposed photoresist to produce master structures for embossing into polymers [6]. Another method for producing a master tool for embossing is the use of anodic oxidation of aluminum [7]. Modern development of embossing comprises the use of nanoimprinting [7,8]. Embossing processes are mostly restricted to flat or slightly curved substrates. Embossing of ARS with an aspect ratio (depth to period ratio) higher than about one seems to be difficult because of deforming problems.

Driven especially by the requirements of photovoltaic, a lot of techniques have been developed during the last years to achieve ARS or porous layers with a low effective refractive index. They comprise porous sol–gel coatings [9,10], single layer coatings produced by microphase separation of polymer mixtures [11], polymer nanoparticle-based porous coatings [12] microcrystalline alumina film with patterned nanostructure [13] and plasma-etched nanostructures on polymers [14,15] and quartz [16,17]. A number of additional processes are mentioned in a recent review article [18]. In most cases the achievable structure depth or layer thickness is limited to about 100 to 200 nm. Some of the layers therefore act rather as a single layer with low index and show only low gradient characteristics. As a consequence, a well-marked reflection minimum occurs in the spectrum and the performance is not at all sufficient for broad spectral ranges.

The focus of this article is on precision optical glass of low refractive index (n 1.52 at 500 nm) where usually antireflective interference stacks are applied and high-end coatings for a higher range of incidence angles are required frequently. Starting from the plasma-etching process for polymers also vacuum deposited small-molecule layers were found to be suitable to generate etched ARS [19]. On the other hand, it would be more difficult to etch glass directly because fluorine compounds are required to remove material. Therefore the idea is to use the organic layers as a carrier to transfer an ARS on top of glass or on top of a suitable interference stack. In this paper, the improvement of the antireflective performance by using layer combinations is investigated by design considerations and by experiments.

2. Experimental details

The organic material 2,4,6-triamino-1,3,5-triazine (melamine) and silica were deposited in a plasma-ion assisted deposition (plasma-IAD) chamber APS904 (Leybold-Optics) [20]. Melamine was evaporated thermally by a filament from a boat. Silica and melamine layers were deposited at a rate of 0.2 nm/s using a base pressure of 5×10^{-4} Pa. Process control of deposition rate and film thickness was achieved with a quartz oscillator. Thin evaporated films of melamine exhibit a crystalline structure. They are transparent in the visible range. The refractive index is 1.82 at 500 nm [19,21]. Variable parameters to obtain different nanostructures on organic materials are: thin seed layers, the ion energy in eV corresponding to the value of bias voltage of ion source APS (Advanced Plasma Source), the oxygen flow and the etching time [22]. In the experiment described here an about 1 nm thick Ta_2O_5 seed layer was deposited on the melamine layer before etching. A

* Corresponding author. Tel.: +49 3641 807 344; fax: +49 3641 807 601.
E-mail addresses: ulrike.schulz@iof.fraunhofer.de (U. Schulz), peter.munzert@iof.fraunhofer.de (P. Munzert), friedrich.rickelt@iof.fraunhofer.de (F. Rickelt), norbert.kaiser@iof.fraunhofer.de (N. Kaiser).

0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2012.11.153

deposition rate of 0.02 nm/s was used to obtain a precise thickness. The etch step was carried out by applying the plasma emitted from the advanced plasma source (APS) which is a direct current (DC) plasma source. Oxygen (30 sccm) was used as the reactive gas and partly ionized by the argon (15 sccm) plasma emitted directly from the source. The typical pressure while running the plasma source was 2×10^{-2} Pa. The ions were accelerated by a self-bias voltage to impinge on the substrate with a maximum energy of 80 eV (at bias 80 V). Starting with an 80 nm thick melamine layer the etching time was 245 s. The silica top-layer was deposited immediately after etching by applying a bias voltage of 80 V.

Reflection and transmission spectra were measured near normal light incidence (6°) using a Lambda 900 spectrophotometer (PerkinElmer) and at higher incidence angle using a goniometer equipped with a polarizer. To obtain the spectra at higher incidence angles, the reflectance and transmission data measured with parallel (p) and perpendicular (s) polarized light were averaged. A Zeiss SIGMA Scanning electron microscope was used to visualize the surface topography of the structures after etching.

3. Results and discussion

3.1. Thin film design considerations

Wavelength ranges exceeding the visible range or for a broader range of incidence angles are still challenging for low-index substrates (n 1.52 at 500 nm). The early work of Minot [4] already showed that the thickness to wavelength ratio d/λ must not fall below 0.5 to realize low reflectance for an incidence angle range of 0° to 60°. Fig. 1 shows the reflectance and the index profile for a step-down design optimized for the wavelength range of 400–800 nm and an incidence angle range from normal incidence to 60°. This system shows better antireflection performance than any possible coating consisting of discrete bulk layers and using bulk silica or MgF_2 as top-layer. But a total thickness of at least 400 nm and an optimal gradient behavior with a fragile open structure would be required to realize a residual reflectance below 1%.

An alternative method to get along with a thinner low-index nanostructured layer is its combination with an interference stack, where also high index layers are incorporated into the multilayer. Initial designs have been evaluated and implemented recently by applying plasma-etched PMMA as a top-layer [21]. Fig. 2 shows a multilayer design optimized for the conditions described before (400 nm to 800 nm, 0°–60° incidence angle). The refractive index profile consists of an arrangement of available coating materials TiO_2 (n = 2.3), Al_2O_3 (n = 1.67), SiO_2 (n = 1.46) and MgF_2 (n = 1.38). For the top-layer an ARS with an effective low-index thickness of 200 nm is sufficient. Thinner nanostructured films are much easier to produce than thick structures. In addition, different specifications regarding wavelength range or incidence angle range could be realized by using the same nanostructured top-layer but different sub-layer stacks. However, design calculations also show that the optical properties of a nanostructured top-layer have to be described with high accuracy because of the high error sensitivity of all single components of combined “hybrid” multilayer.

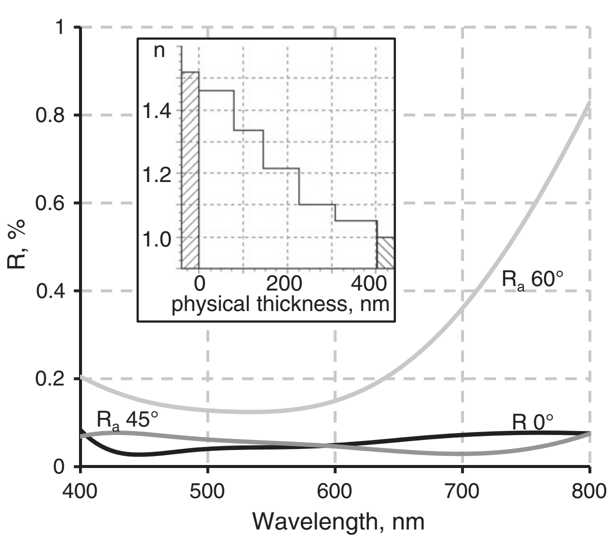

Fig. 1. Refractive index profile and reflectance R (average polarization at 45° and 60°) for a 5-layer step-down design, substrate refractive index of 1.52.

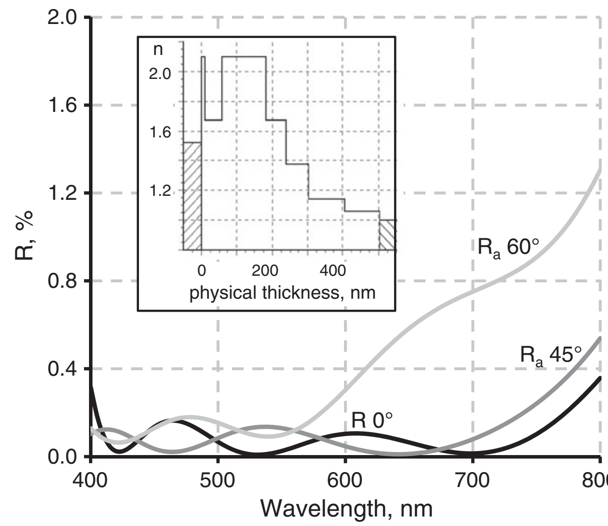

Fig. 2. Refractive index profile and reflectance R (average polarization at 45° and 60°) for an interference multilayer with low-index top-layer. The thickness of the low-index fraction on top is about 200 nm.

3.2. Properties of a nanostructured silica–melamine–silica combination

As a first step to complex multilayers some investigations on a simple hybrid system comprising one nanostructured organic layer and two surrounding silica layers have been conducted. The whole system was realized in a conventional plasma-IAD vacuum chamber within less than 1 h process time. Plasma-etched melamine layers consist of columnar-shaped nanostructures and exhibit only low gradient character [21]. The unprotected open surface is fragile (Fig. 3). Former experiments on etched polymers had shown that a more or less closed silica film on top of ARS is very helpful to provide the system a better environmental and mechanical stability [22]. In the hybrid system, a silica layer was applied as a first step down from the substrate refractive index 1.52 to the silica index 1.46. To assist an about 80 nm thick nanostructured melamine layer optically, the thickness of the silica layers was chosen to be 70 nm. The relative dense melamine structure obtained with a tantala seed layer was simulated by using three sub-layers with refractive indices of 1.41, 1.35 and 1.25 respectively. A 40 nm silica top-layer was deposited to cap-off the surface nearly completely (see Fig. 4). This layer was taken into account in the simulation only simplified with a homogeneous refractive index of 1.41. The refractive index profile used in a first model and the calculated reflectance are shown in Fig. 4a. Slight variations of the model regarding the composition of the gradient layer have a significant influence on the reflectance especially at higher incidence angle as shown in Fig. 4b for model 2. In fact, the gradient part consists of porous silica (bulk index 1.46) which is growing partly into the open melamine structure with material index of 1.8. As a third component hollows are disclosed in the structure. Because of this complexity it seems that it is not possible to describe the deposited gradient layer accurately. In fact, the residual reflectance achieved experimentally (Fig. 4c, backside reflectance removed by calculation) differs from that of both models. Fig. 4d shows a SEM picture of a