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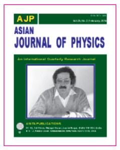

Encapsulation of optical gratings using nanoporous alumina layers

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(Dedicated to Professor Wolfgang Kiefer on the occasion of his 75th birthday)

In this work, we describe a method to encapsulate optical gratings with nanoporous Al_2O_3. The encapsulation process consists of covering a grating, filled with a sacrificial material, by an organic-inorganic thin alucone layer. The element is than heated upto 400 °C to remove the organic component from the alucone film. The nanoporous Al_2O_3 film, formed after the removal of the organic component acts as a diffusion layer for the decomposition products of the sacrificial material. The complete removal of the sacrificial material was confirmed by energy dispersive x-ray spectroscopy (EDX).

Keywords: Optical gratings, Energy dispersive x-ray spectroscopy (EDX).

1 Introduction

Diffraction gratings are essential components in optical systems to manipulate the propagation of light. Generally, periodically nanostructured elements are used to diffract the light. The function of the gratings is highly dependent on the material of the element, on the period, the width and the depth of the nanostructures as well as on the wavelength of the incident light [1]. Depending on the mentioned parameters, the diffraction gratings are widely used in monochromators, spectrometers, laser systems, etc. [2-5].

Even though optical gratings highly enhance the performance of optical systems, they have a main drawback of being mechanically not as stable as unstructured optical elements. Moreover, the grating structures are sensitive to contaminations (such as organic rests or particles), which in contrary to e.g. thin film coatings cannot be cleaned or removed due to the high aspect ratio of the surface. The contamination or damage of the nanostructures strongly deteriorates the optical function of the optical elements with time.

To protect the nanostructures against environmental influences, different encapsulation methods were proposed. Nishii *et al* covered binary gratings with thin SiO_2 layers by plasma enhanced chemical vapor deposition (PECVD) at 400°C substrate temperature [6]. However, the PECVD deposition partially fills the upper part of the grooves, which in turn can highly reduce the efficiency of the element. Direct bonding is another method which was applied to protect nanostructures [7,8]. In this case, the structured wafer and an unstructured wafer of the same material are directly bonded under compressive pressure. In order the encapsulation through direct bonding to be successful, both surfaces must be highly clean and very smooth. The bonding process is very challenging and time consuming, since any small defect, contamination or differences in the height profile of the structures will strongly disturb the optical function.

Recently, Ratzsch *et al* proposed a new encapsulation process based on the selective removal of a sacrificial material by wet chemical etching [9]. The encapsulation was realized by first filling the gratings with a sacrificial material. Afterwards, the excess material on top of the grating was removed and a thin SiO_2 cover layer was deposited using atomic layer deposition (ALD). Narrow grooves were created in the cover

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layer to remove the sacrificial material. At the last stage, the sacrificial material was removed by selective chemical etching in phosphoric acid solution. The drawback of this method is the necessity to pattern the top SiO_2 layer by complex etching techniques even though the period of the upper grooves is several hundreds of nanometer.

In this work, we have deposited hybrid organic/inorganic alucone alloys using atomic layer deposition (ALD) and molecular layer deposition (MLD). Calcination of these alloys at elevated temperatures leads to the formation of nanoporous Al_2O_3. The nanoporous Al_2O_3 was used as diffusion layer to encapsulate optical gratings. The gratings were first filled with a sacrificial material (polymer resist) and covered by a thin alucone layer. Afterwards, the sacrificial material was completely removed by heating up to 400°C. Hence, the grating structure is finally protected by a thin capping layer of Al_2O_3 that can be further reinforced by standard physical vapor deposition techniques.

2 Experimental methods

2.1 Atomic layer deposition (*ALD*) *and molecular layer deposition* (*MLD*)

Atomic layer deposition (ALD) is a powerful thin film coating technique allowing to precisely control the film thickness of inorganic coatings based on sequential self-limiting surface reactions [10,11]. Similar to ALD, molecular layer deposition (MLD) enables growing completely organic or organic-inorganic hybrid polymer thin films typically using bi- or multifunctional monomers [12,13]. One class of such hybrid polymers are alucones which are grown with MLD using trimethylaluminium (TMA) as inorganic and ethylene glycol (EG) as organic constituent (Fig 1) [14]. By changing the number of MLD cycles, alucone thin films with desired film thickness can be deposited.

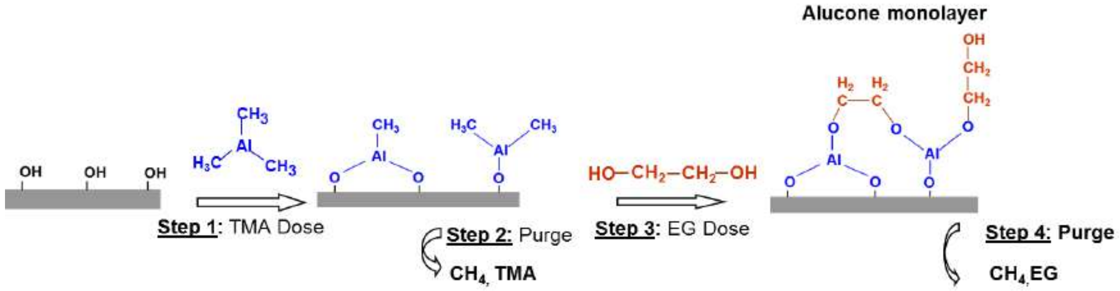

Fig 1. Schematic view of 1

The Oxford Instruments Opal ALD open load system equipped with three precursors and a separate H_2O input was used for these experiments. The alucone alloy films were deposited using alternating sequences of TMA/H_2O for ALD Al_2O_3 and TMA/EG for MLD alucone. The Al_2O_3 was deposited using 10 ms TMA dose and 30 ms H_2O with 7 s purge times between each precursor dose. The alucone MLD films were deposited with 10 ms dose and 7 s of purge times for TMA and 2 s EG dose with subsequent purge of 15 s. After the EG purge, 10 s of the chamber purge was done to make sure that the whole unreacted EG molecules get out of the reaction chamber before the next TMA dose entry. All depositions were done at 150°C substrate temperature.

2.2 Characterization techniques

The thickness and the refractive index of the films were obtained by *ex situ* spectroscopic ellipsometry (J A Woollam Co., Inc.) in the spectral range of 250–1700 nm. The experimental data were analyzed with Complete EASE software provided with the equipment. The measured data of the dense film was fitted to a Cauchy function and of the nanoporous films to effective medium approximation (EMA). For the nanoporous samples the fit was done from 400 nm to get an improved fit.

Scanning electron microscopy (SEM) images and energy dispersive X-ray analysis (EDX) for chemical characterization were recorded with ultra-high resolution Hitachi High-Technologies (Hitachi S-4800) scanning electron microscope. The scanning time of the sample during EDX analysis was 5 minutes.

Neon 60 Cross Beam focused ion beam scanning electron microscopy (FIB-SEM) was used to get the cross-sectional micrographs of the encapsulated grating.

2.3 Encapsulation process

To encapsulate optical gratings with nanoporous Al_2O_3, a manufacturing process was developed consisting of 4 steps. The schematic view of the encapsulation of the gratings using MLD/ALD alucone alloy layers is shown in Fig 2.

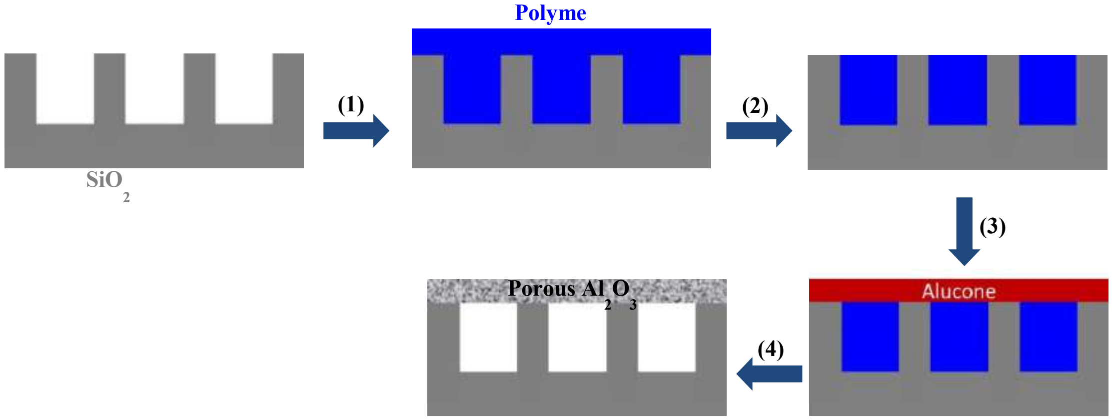

Fig 2. Schematics of the encapsulation process. **(1)** Spin coating of a polymer sacrificial layer, **(2)** planarization, **(3)** deposition of MLD/ALD alucone alloy layer, **(4)** removal of the sacrificial layer by annealing.

In the first step (**1**) the grating was filled with a sacrificial material by spin coating. As a sacrificial material, an organic polymer material was chosen (resist AZ1505), which is unstable at high temperatures. This ensures that during heating the sacrificial material will completely decompose and will be easily removed from the grooves. The spin coated polymer does not only fill the grooves but also covers the grating bars. Therefore, in the step (**2**) the excess amount of the material from the top of the grating is removed. This was done by reactive ion beam etching (RIBE) using Ar^+ ions. Afterwards, (step (**3**)) the deposition of thin alucone alloy layer on the planarized surface by MLD/ALD was carried out. To ensure a better stability of the cover layer, 1 cycles of ALD Al_2O_3 was inserted after every 5 cycles of MLD alucone deposition. In the last step, the element is heated up to 400 °C to remove the organic constituents from the alucone layer and the sacrificial material from the grooves.

3 Results and Discussion

In recent years, nanoporous Al_2O_3 was produced by heating MLD alucone layers at elevated temperatures [15,16]. These layers were used as diffusion layers to develop highly efficient composite membranes for H_2 separation [17] and for producing Cu oxide nanoparticles [18,19]. Moreover, due to the porosity, the layers were shown to have much lower refractive index than the refractive index of the compact layers [20]. Nanoporous Al_2O_3 layers with a refractive index of 1.34 were realized. Here, we apply these nanoporous thin films as diffusion layers to encapsulate conventional binary gratings.

Following the scheme shown in Fig 2, we encapsulated binary SiO_2 grating with a period, groove width and groove depth of 400 nm, 300 nm and 850 nm, respectively. After spin coating of the sacrificial polymer and subsequent removal of the excess material, 85 nm alucone/Al_2O_3 layer was deposited by MLD/ALD. Afterwards, the element was heated from room temperature up to 400 °C at the rate of 10 °C/min and left at this temperature for 45 h. Figures 3(a) and (b) show a top and cross-sectional view of the encapsulated grating, respectively.

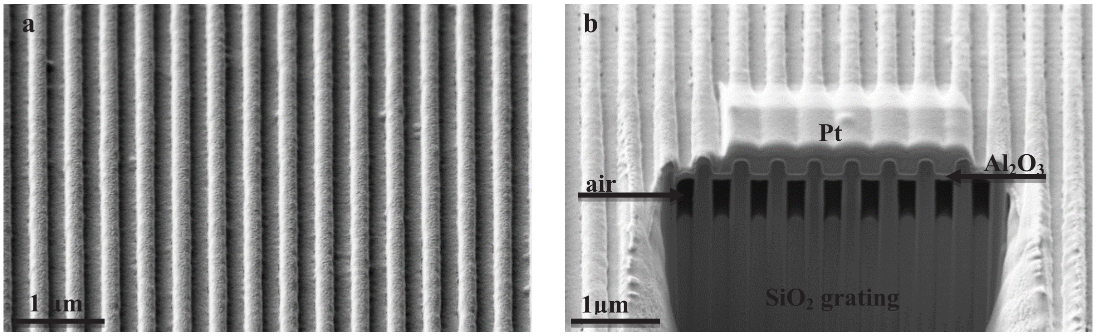

Fig 3. Focused ion beam scanning electron microscopy (FIB-SEM) micrographs of the binary SiO_2 grating encapsulated with nanoporous Al_2O_3, (a) top and (b) cross-sectional view.

As a result of the heat treatment, the organic part of the alucone layer was decomposed and removed leaving nanoporous Al_2O_3 thin layer as a cover layer. Simultaneously, the sacrificial polymer material also decomposes to volatile gasses (CO_2 and H_2O mainly), which then diffuse through the porous Al_2O_3 layer. As it can be seen from the top view image in Fig 3a, the removal of the organic components does not destroy the cover Al_2O_3 layer, if the alucone film is thick enough. If the capping layer was deposited with 36 nm alloy thickness, instead of 85 nm, the cover layer was not stable any more but showed cracks all over the surface. The encapsulation was also not possible, if the alucone deposition was carried out directly on top of the sacrificial layer, before removing the excess material. This could be caused by a very high pressure which arises due to the decomposition of the excess polymer amount compared to the amount of the polymer in the grooves. The sinking on the top is due to the shrinkage or partial removal of the sacrificial AZ layer during ALD/MLD deposition. This can be improved by choosing another polymer material as sacrificial layer, which is insensitive to the ALD/MLD processes.

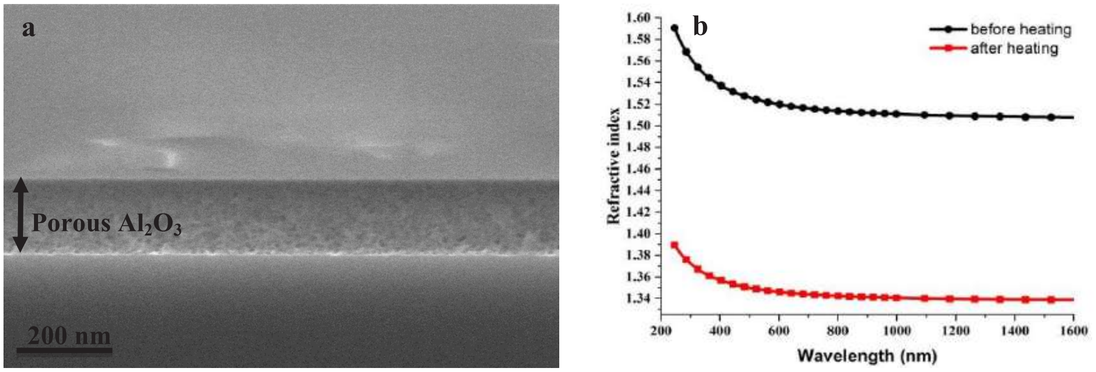

Fig 4(a). The SEM cross-sectional view of the alucone layer after heat treatment, (b). the effective refractive index spectra of alucone alloy layer before and after heat treatment.

To record a good cross-sectional image by focused ion beam scanning electron microscopy (FIB-SEM) and to protect the sample, deposition of Au (as conducting layer) and locally Pt (as protection layer) was necessary on the encapsulated grating. Under the burden of these layers, the nanoporous Al_2O_3 layer is compressed so that the porous nature of the cover layer cannot be observed in Fig 3b. The nanoporous nature of the Al_2O_3 layer after heating the alucone layer is revealed in Fig 4a. In this case, the MLD/ALD deposition was done on Si(100) substrate, and the micrograph was taken with scanning electron microscopy (SEM) without any further deposition. Moreover, the decrease of the refractive index of the film after heat treatment from 1.52 to 1.34 at the wavelength of 632.8 nm confirmed the porous nature of the Al_2O_3 film (Fig 4b).

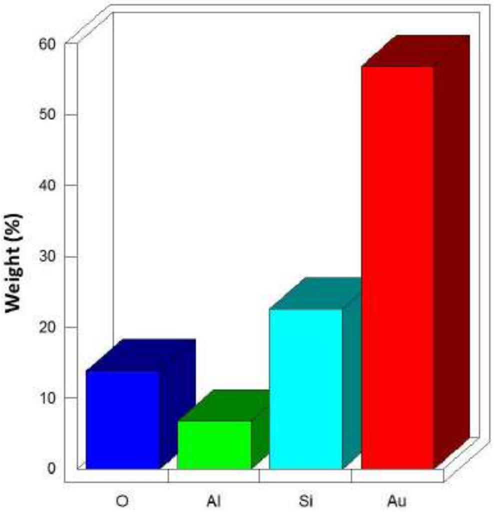

Fig 5. Energy dispersive x-ray spectroscopy (EDX) of the SiO_2 grating encapsulated with Al_2O_3.

Energy dispersive x-ray spectroscopy analysis (EDX) confirmed that the sacrificial polymer material was completely removed from the grating grooves. Figure 5 shows that only 4 elements could be detected: O, Al, Si and Au. The Au signal comes from the conducting layer deposited to obtain the FIB-SEM micrograph. The Si signal is caused by the substrate (SiO_2 grating), whereas the cover Al_2O_3 gives rise to the Al and partially to the oxygen (O) signal. The carbon (C) signal that might arise from remaining organic component in the alucone layer or from the resist material could not be detected after thermal treatment.

4 Conclusions

In summary, we have developed a versatile route to encapsulate optical gratings by heat treatment of the nanostructured elements covered by MLD/ALD deposited alucone/Al_2O_3 alloy layer. One cycle of ALD Al_2O_3 was inserted after every 5 cycles of MLD alucone, to avoid excessive collapse of the film after the removal of the organic constituents. The evolution of the porosity in the cover layer and the removal of the sacrificial polymer material could be achieved by simple heat treatment up to 400 °C in air. The EDX measurements showed no signal from carbon (C) after heating, indicating the complete removal of the sacrificial polymer material from the grooves. Further experiments will be carried out to improve the quality of encapsulation by preventing the sinking of the cover layer and to apply this encapsulation method to functional optical elements.

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This Communication is dedicated to Professor Wolfgang Kiefer on the occasion of his 75th birthday.

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