Transparent MgF$_2$-films by sol–gel coating: Synthesis and optical properties

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Abstract

Dielectric, anti-reflective or high reflective systems consist of low and high refractive index layers. Common systems are oxides. The preparation of low refractive index MgF$_2$-films of optical quality by means of an anhydrous low temperature sol–gel synthesis is presented. The MgF$_2$-sol is prepared by spin-coating on silicon and glass substrates. Various film thicknesses between 20 nm and 435 nm have been deposited. It has been shown that the thickness increase is proportional to the number of coating steps. The deposited MgF$_2$-films consist of 10 nm to 20 nm large nanoparticles and have smooth surfaces with an average roughness ($R_a$) of (1.7±0.3) nm. The optical constants $n$ and $k$ of the films are in agreement with the literature data of bulk-MgF$_2$.

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1. Introduction

Dielectric, anti-reflective, or high reflective multilayer systems consist of alternating dielectric layers of low and high refractive index. Currently, the most common materials are oxides like SiO$_2$ as low refractive index material ($n_{500}=1.46$) and TiO$_2$ (up to $n_{500}=2.40$) or Ta$_2$O$_5$ ($n_{500}=2.10$) as high refractive index materials. These oxide systems are mostly produced by physical vapour deposition (PVD) like evaporation or sputtering, depending on the size and performance requirements of the optical device. Despite the fact that metal oxides (and fluorides) can be synthesised by high temperature sol–gel technique, these processes are usually not applicable to most of the substrate materials used for optical devices because of process temperatures beyond 300 °C.

Oxide systems offer a high transparency in the near IR-, visible and near UV spectral range. Due to increasing absorption in the UV, oxides are limited to the near UV (e.g. down to 210 nm for SiO$_2$). Metal fluorides have a better transparency in the UV, e.g. MgF$_2$ is sufficiently transparent for optical applications down to 120 nm. A further advantage of MgF$_2$ is its low index of refraction ($n_{500}=1.38$).

The general procedure of the low temperature sol–gel synthesis of MgF$_2$ has been reported earlier [1]. In contrast, the low temperature sol–gel synthesis of a high refractive index material is more sophisticated. A candidate seems to be PbF$_2$ with a refractive index of $n_{500}=1.75$. Both materials (MgF$_2$ and PbF$_2$) might thus be appropriate for optical multilayers made by low temperature sol–gel synthesis. However, one of the most important parameters of optical multilayers, i.e. the difference of the refractive indices $\Delta n$, is still much lower in the case of these fluorides ($\Delta n=0.37$) as compared to the most commonly used oxides ($\Delta n=0.64$ and $\Delta n=0.94$). Other candidates (besides PbF$_2$) for high reflective fluoride materials replacing the problematic ThF$_4$ are YF$_3$, ZrF$_4$, or HfF$_4$. All of these materials show a significant index contrast compared to MgF$_2$, AlF$_3$, or Na$_3$AlF$_6$. These films are deposited by PVD methods which are quite expensive compared to the sol–gel process. For high temperature sol–gel applications, the fluorination agents are fluorinated organic compounds which pyrolize during annealing. These calcination temperatures are above 400 °C and hence not suitable for organic polymer substrates.
The non-aqueous sol–gel synthesis method for metal fluorides that we have developed allows for the preparation of MgF₂-films at low temperatures [1]. The MgF₂-sol obtained by this method are prepared from a suspension of magnesium methoxide in methanol and a non-aqueous HF solution in methanol [2]. The molar ratio of magnesium alkoxide and HF is kept at 1:2 and the sol concentration can be adjusted by altering the amount of solvent used. This MgF₂-sol can be deposited on silicon or glass substrates using spin- or dip-coating. After a moderate thermal treatment (100 °C–300 °C), transparent and strongly adhering MgF₂-films are obtained. This coating process is very simple and cheap in comparison to the common, very complex PVD-methods and corrosive gases such as HF and F₂ are not needed. Because the calcination temperature of the coatings can be below 150 °C, this method is suitable for temperature-sensitive substrates like organic polymers and therefore facilitates other fields of application.

In this paper, we present the deposition of MgF₂-films of optical quality by means of an anhydrous low temperature sol–gel synthesis using MgF₂-sols and their characterization by light microscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and spectroscopic ellipsometry (SE).

2. Experimental section

The MgF₂ precursor solution are prepared from a suspension of magnesium methoxide in methanol and a non-aqueous HF solution in methanol. The molar ratio of magnesium alkoxide and HF is maintained at 1:2. The concentration of magnesium methoxide in the precursor solution was varied as indicated in Table 1. The Si substrates were cleaned in an ultrasonic bath and etched with the RCA method [3], they were then wetted with the MgF₂-sol and spin-coated. A Spin-Coater KW-4a from Chemat Technology was used for this process. The coatings were prepared at 5000 rpm for 40 s. After each coating step, the substrates was dried for 30 min at 100 °C. The number of coating/drying cycles is described in Table 1. The final calcinations were carried out for 2 h at temperatures of 100 °C or 300 °C in air.

The transmission electron microscopy (TEM) images were taken with a JEM400FX from Jeol with an operating voltage of 400 kV. The sample was first coated with gold (10 nm) and platinum (1 μm). A TEM lamella was then cut with the focussed ion beam FEI Strata 200 xP (Ar⁺-ions at an operating voltage of 30 kV). The EDX measurements were done with TN5402 from Tracor during the TEM measurement. The AFM measurements were done in accordance with the description of Heyde [4] and with the apparatus described therein. The ellipsometric measurements were carried out with a variable angle UV–vis spectroscopic ellipsometer (VASE) from J.A. Woollam Co. Inc. in the wavelength range between 250 nm and 800 nm. The measurements in the wavelength range between 130 nm and 500 nm were done with a VUV–XUV ellipsometer setup which was installed at the 3 m-NIM beam line at BESSYII [5]. In order to analyse the ellipsometric data with the program WVASE from the manufacturer, the data sets of the VUV- and vis-range had to be combined to a consistent data set. For the calculation of the indices of refraction n and the indices of absorption k, a generalised Kramers–Kronig consistent oscillator model of Gauss- and Lorentz-form oscillation functions was used [6]. The film thickness was calculated with the data set in the visible range (250–800) nm using the CAUCHY model.

3. Results and discussion

Starting from MgF₂-sols obtained by a reaction of an alcoholic suspension of Mg(OR)₂ with a solution of anhydrous

<table>
<thead>
<tr>
<th>Concentration of the sols [mol/l]</th>
<th>Number of coating steps</th>
<th>Film thickness [nm]</th>
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</thead>
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<tr>
<td>0.15</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
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<td>3</td>
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<td>101</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>336</td>
</tr>
</tbody>
</table>

Fig. 1. AFM image of a three step coated MgF₂-layer on a silicon wafer calcined at 300 °C.

Fig. 2. TEM cross section image of a six step coated MgF₂-layer on a silicon wafer calcined at 100 °C.
HF in alcohol, planar surfaces were coated with a spin-coater. Depending on the concentration of the MgF₂-sol, different film thicknesses were obtained with a single coating step. The thickness of a single coating step varies between 20 nm and 120 nm. Total film thicknesses between 20 nm and 435 nm can thus be achieved (Table 1), whereby a roughly linear relationship between film thickness and number of coating steps was observed. The layer thickness was derived from the ellipsometry data in the visible range. A few percent thickness inhomogeneity was achieved over a 2” silicon wafer.

Light microscopy images of the MgF₂-films show the formation of a homogeneous surface with a few small cracks caused by dust particles under ambient conditions which are already visible before the annealing step. A further crack formation may be induced by the thermal stress during calcination. Consequently, it is very important to carry out coating under clean-room conditions. AFM-images of the surfaces (Fig. 1) confirm the formation of homogeneous surfaces with an average roughness of (1.7±0.3) nm consisting of nanoparticles of a diameter from 10 nm to 20 nm.

Repetitions of the coating process result in macroscopically tight, strongly adherent, and transparent layers. The single coating process is detectable by TEM as shown for a cross-section TEM-image of a six-step MgF₂-film (Fig. 2). The linear dependence between film thickness and number of coating steps is also confirmed by this image. The MgF₂-nanoparticles in the layer are predominant amorphous but partially fine crystalline with crystallite sizes from 2 nm to 5 nm.

By EDX, magnesium and fluorine were detected as the main constituents of the films. Traces of carbon and oxygen were also found, but these can be attributed to contamination during the lamella preparation process and to the mounting of the lamella on a graphite sample holder.

The optical constants of the sol–gel MgF₂-films determined by ellipsometry are in good agreement with literature values of bulk-MgF₂ (Fig. 3) [7]. The film indices of refraction are smaller than those of the bulk phase due to a lower density of the MgF₂-films as compared to the bulk material [8,9]. The absorption of the MgF₂-layers in the UV appears to be higher than literature data suggest. Because of the measuring setup of the VUV-ellipsometer which has no ability to measure at multiple angles of incidence or with a retarder, the ellipsometry data in the UV-range is not adequate enough to clearly interpret this absorption. Feasible reasons for the absorption could be organic impurities which originated from an incompletely removed solvent. An alternative explanation for this fact could be an apparent absorption due to a loss of intensity by in-plane scattering on the nanoparticles in the layer.

4. Conclusions

The results show that MgF₂ layers with qualified optical properties can be deposited by this sol–gel synthesis on planar surfaces. Further optimisation of this process may allow the preparation of thin films with defined thicknesses for use in optical multilayer systems. Low calcination temperatures during the post-treatment of the layers permit the deposition of heat sensitive substrate materials. In combination with high refractive index metal fluorides like HfF₄ or PbF₂ which are also available by this sol–gel synthesis, alternatives for optical multilayers with improved properties in the UV compared to oxides emerge. The formation of high refracting metal fluoride coatings with the same optical quality therefore is in the focus of present activities.

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