Magnetron discharge sputtering for fabrication of nanogradients optical coatings

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Abstract. The technology of the middle frequency pulse reactive magnetron sputtering for fabrication of nanogradients optical coatings with smooth variation of refractive index was developed and studied. The technology is based on programmable motion of a substrate over two magnetrons with targets of different materials. The feature of the deposition process is a constant composition of reactive gas medium and an invariable magnetron operation mode. To realize this technology, an automatic computer-controlled sputtering system additionally comprising a gas discharge activator of reactive gas (oxygen) and an in situ optical monitor-spectrovisor has been built. The dielectric oxide-based nanogradient coatings of photon-barrier type were successfully fabricated. The obtained results confirm the high potential of the middle frequency pulse reactive magnetron sputtering of silicon and metal targets for fabrication of nanogradients dielectric optical coatings with excellent properties.

1. Introduction

Coatings on various optical elements/substrates play an important role in optics and photonics. They are used for improving spectral, reflective or antireflective, angle, polarization, and phase properties; in particularly, very wide working spectrum band and wide operation angle may be provided. Typically, optical coatings are multilayer thin film interference structures with a stepwise periodic variation in refractive index \( n \). In recent years in optics and laser technology, the increasing attention has been paid to coatings with a smooth, gradient (rather than abrupt) variation in index \( n \), such as antireflective coatings and rugate rejection filters [1, 2]. The smooth variation in \( n \) values leads to the improvement of many characteristics of coatings including the excellent matching of wave impedance, thermomechanical strength and laser damage resistance thereof. When the refractive index \( n = n(z) \) continuously, gradually distributed by a certain law within a medium, the latter is called as gradient one. If axis \( z \) is the direction of light propagation (it coincides typically with the normal to substrate surface), we have the so called longitudinal \( 1D_z \) gradient [2]. If change of \( n \) values occurs on distance less than 100 nm, such coating should be called as nanogradients one. Various refractive index profiles

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Nowadays, the transformation optics arises as a new direction in optics where the effective control of radiation is conducted using a gradient medium of metamaterials (composites undergoing an electromagnetic reaction), which have been used to show the invisibility effect (the “invisibility cloak” effect) [3].

In order to fabricate a gradient coating, we need materials with variable $n$ values. However, there is a limited range of natural optical materials with discrete $n$ values; therefore, to obtain intermediate $n$ values, it is necessary to prepare mixtures of available materials or derivatives thereof (nonstoichiometric oxides, oxynitrides, etc.) directly on the substrate by depositing the appropriate materials in atomized form. There are several ways to provide gradient variation in the refractive index $n$ [2]. Among them, the common method is electron beam co-evaporation of two source materials but it is associated with the complexity and fundamental limitations of synchronized nonstationary evaporation of refractory materials from highly localized sources that constrains the industrial fabrication of precision nanogradient optical coatings. The other method is ion beam co-sputtering of several source materials but this method gives very low productivity. Meantime, the ion sputtering in magnetron discharge is able to provide very high sputtering rate and widely employed in industry. The magnetron discharge is a low pressure gas discharge in crossed electric and magnetic fields where the solid cathode serves as target sputtered by ions from discharge plasma. The deposition in magnetron discharge gives dense pore-free thin film coatings of excellent quality with good adhesion. However, the deposition of nanogradient optical coatings by the magnetron method is a relatively new field of technology [2] and needs intensive research and development for its implementation. The aim of the given work is examination and approbation of our recently developed magnetron sputtering method for deposition of dielectric layers with variable refractive index. As an example, we choose the process for fabrication of nanogradient optical coating of the “photon barrier” type.

2. Magnetron discharge sputtering apparatus and procedure for deposition of nanogradient optical coatings

The diagram of an automatic computer-controlled setup with a two-magnetron system for the ion sputtering of two materials in a reaction medium is shown in figure 1. In our experiments, targets of Si and metal (Nb, Ta or Ti) were sputtered in an argon atmosphere with an oxygen additive. The arrows above magnetrons M1 and M2 indicate the direction of propagation of the sputtered target materials; one can see some part of sputtered materials is captured by substrate S with coating formation on its lower surface.

![Diagram of two-target magnetron sputtering system for deposition of a nanogradient coatings of a mixtures of two oxides of two materials](image)

Figure 1. Diagram of two-target magnetron sputtering system for deposition of a nanogradient coatings of a mixtures of two oxides of two materials (the right picture shows top view): (Ar) flow of inert sputtering gas Ar; (A) activator of reactive oxygen; (L) laser; (M1, M2) sputtering magnetrons with Si and metal (Nb, Ta, Ti) targets; (Mt1, Mt2) optical parts of in situ monitoring system; (O₂) flow of reactive gas O₂; (S) rotating substrate, which can move along the main axis (bold line); the oval racetrack zones on the magnetron targets are the sputtered areas; the arrows above the magnetrons indicate the direction of propagation of the sputtered target material.
The composition of the coating material deposited on substrate S is determined by the substrate position (that is distances \( X_1 \) and \( X_2 \)), the specified algorithm of the space–time motion of substrate S over magnetrons M1 and M2, and the electric power of the magnetrons. Depending on the composition, the refractive index \( n \) value of the coating varies. To prepare a coating with the longitudinal 1D\(_2\) gradient of \( n \), it is necessary to provide a high uniformity of distribution of the \( n \) value along the radius of the substrate; therefore, the \( X_1 \) and \( X_2 \) distances are selected to meet the requirement for obtaining a maximum uniformity of the coating thickness along the radius of the rotating substrate with a minimum cross sputtering of the magnetron targets. To synthesize a stoichiometric dielectric coating with minimum optical losses, the reactants – the sputtered and deposited metals and the reactive gas (oxygen) – should be chemically activated. In the given setup, the activation occurs owing to the physical-chemical processes in the magnetron discharge plasma, the additional activation of oxygen in a special gas discharge device (activator A) through which the gas \( O_2 \) is fed onto the substrate, and the exposure of the substrate to ultraviolet laser L radiation.

The deposition and synthesis of the coatings were controlled by in situ optical monitoring of the coating properties using spectrovisors Mt1-Mt2. The optical thickness, refractive index, and spectral characteristics of the growing layer were determined.

The important issue is the choice of parameters of electrical power and gas supply of the magnetron system. Different approaches to power and gas regulation are known to be used for obtaining gradient coating [2]. We consider the most suitable way to ensure the stability and reproduction of the precision deposition process is keeping the invariable regime of power supply and constancy of gaseous parameters during the sputtering process. This provides constancy of temperature in the deposition chamber and rate of chemical reaction on the substrate surface. In the end, it means that the current composition of the synthesized coating material is controlled only by the law of substrate motion above the magnetrons.

The thickness of partial layer deposited at the given substrate position is determined by dose of captured atoms sputtered from magnetron targets. Each dose can be evaluated as the product of sputtered atom flow captured by the substrate and duration of substrate exposure by this flow. The exposure duration is the time period when the substrate is in the given position. The refractive index of the growing coating is determined by the ratio of partial doses of captures atoms from the two magnetron targets.

Thus, the deposition procedure is based on the variation of the substrate position \( X_1 \) (or \( X_2 \)) and the exposure duration in the given position under computer control; herein the powers of magnetron discharges and values of gas parameters in the deposition chamber remain constant. Such approach ensures the stable sputtering rates of both the magnetrons in reactive gas medium.

Before the elaboration of computer control program, the deposition process has to be calibrated: the coating deposition rate and the refractive index \( n \) value are experimentally determined for each possible substrate positions at the given electrical powers of two magnetron discharges. Then, the computer control program describes step-by-step the trajectory and the time characteristic of substrate motion over the magnetron targets along the main axis shown in figure 1. To obtain the refractive index profile \( n(z) \) in the coating with the minimal value, corresponding to the index of SiO\(_2\), and the maximum value, corresponding to the index of other metal oxides, the computer provides movement of the substrate step-by-step from the position above 1\(^{st} \) magnetron (M1) with Si target (\( X_1 = 0 \)) to the position above 2\(^{nd} \) magnetron (M2) with metal target (\( X_2 = 0 \)), then to the position over 1\(^{st} \) magnetron, and so on, if a periodical gradient structure is in need. The aforesaid calibration curve, presenting the calculated dependence of refractive index \( n \) upon the distance \( X_1 \) along the trajectory of silica substrate motion is shown in figure 2. The substrate diameter was 3 cm. The electrical and gas conditions during the calibration process are described below. Values of \( n \) from this curve were verified by means of ellipsometry of the single layer. Thus, the computer program contains information on the duration of each exposure in each position of the substrate accordingly to the prescribed refractive index profile.
For sputtering Si target and the second target of metal, the middle frequency (22 kHz) pulse mode of magnetron power supply has been used. Such mode excludes arcing on the magnetron targets in reactive gas medium. The arcing is caused by formation and electrical charging of dielectric films on the targets but they are discharged by plasma electrons during pause between magnetron current pulses. The calibration (see figure 2) of the deposition apparatus and fabrication of the nanogradient optical coating were fulfilled at the following magnetron operation conditions: the average current of both the magnetron discharges was 0.5 A (the discharge voltages were 380 V for Si target, M1, and 580 V for Ta target, M2), the total pressure of argon-oxygen gas mixture in the chamber was about 0.1 Pa. The substrate was prepared from quartz glass $K_8$ with the refractive index $n_s = 1.51$. The calibration has indicated indeed that the minimal value of the refraction index ($n_m \approx 1.5$) was obtained when the substrate was above the magnetron M1 with Si target; the maximum value of the refraction index ($n \approx 2.1$) was obtained when the substrate was above the magnetron M2 with Ta target. The process duration for deposition of gradient layer with thickness $d = 140 \text{ nm}$ was about 1000 sec.

3. Results of nanogradient optical coatings deposition
Using the above described magnetron sputtering setup and the computer-controlled deposition process, the assigned periodical concave profile of variation in the refractive index $n(z)$ over the depth of the coating (figure 3) has been prepared by depositing a mixture of synthesized silicon and tantalum oxides on a quartz glass substrate via pulse sputtering of two targets (Si and Ta) in the oxygen medium. The shape of the given $n(z)$ profile has been proposed and theoretically grounded by Prof. A. B. Shvartsburg [4] as having heterogeneity-induced dispersion and photon barrier properties in the visible spectral range. The profile comprises five periods of variation in the $n$ values.

![Figure 3. Nanogradient five-period profile of $n(z)$ for coating from SiO$_2$+Ta$_2$O$_5$ mixture.](image)

Figure 4 shows the calculated and experimentally measured transmission spectra of the fabricated nanogradient coating; good matching of these spectra suggests that the real profile of variation in the refractive index over the depth of the coating is close to the assigned $n(z)$ profile. One can see such
coating may be considered as a nanogradient rejection filter with band-stop, \textit{i.e.} as a photon barrier, in the limited band in visible spectral range, and there is the wide band antireflection effect in the near infrared range.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4}
\caption{Calculated (dashed line) and experimental (solid line) transmission spectra of the nanogradient coating of SiO$_2$+Ta$_2$O$_5$ mixture with five-period \(n(z)\) profile.}
\end{figure}

Some other properties of the fabricated coating may be mentioned. The coefficient of optical losses is less than $5 \times 10^{-5}$. The coating is resistant to laser radiation with power density $W > 10^9$ W/cm$^2$ for $\lambda = 1064$ nm, $\tau = 10$ ns and the combination of thermal cycling ($\Delta t = -60/+70$°C, 100 cycles) with UV exposure at power density $W > 100$ W/cm$^2$ for $\lambda = 300$ nm, as well as to 3500 cycles of heating up to +180°C with 5 minutes exposure and cooling down to −190 °C (immersion into liquid nitrogen) with 1 minute exposure.

4. Conclusions
The obtained results confirm the middle frequency pulse reactive magnetron sputtering of silicon and metal targets is a perspective method for fabrication of precision nanogradient dielectric optical coatings with excellent spectral properties, in particular, with the photon barrier effect in visible spectral range and the wide band antireflection effect in the near infrared range. The main feature of the proposed technology is the programmable motion of the substrate over two magnetrons with targets of different materials at a constant composition of reactive gas medium and an invariable magnetron operation mode. Such technology is not very complex and may be easily adopted to industrial application. The promising application of this technology is fabrication of gradient optical metamaterials [4, 5], high performance solar cells and devices based on transformation optics. The dense pore-free microstructure and good adhesion of the coating, which are typical for magnetron sputtering, and absence of the internal sharp boundaries separating the layers with high and low \(n\) ensure the resistance to environmental factors, including thermomechanical ones. The nanogradient microstructure of the coating ensures the resistance to high power laser radiation damage.

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