Optical Coatings (Nb_2O_5, Ta_2O_5 and WO_3) for LAC-Applications Obtained by DC Quasireactive Magnetron Sputtering of Ceramic Sputtering Targets

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ABSTRACT

Refractory metal oxides show interesting properties for optical thin film applications such as high refractive indices and low extinction coefficients (Nb_2O_5, Ta_2O_5, ZrO_2), electrochromic behavior (WO_3) or electrical conductivity (MoO_2). As with most metal compound materials, such films are usually deposited by reactive magnetron sputtering of metallic sputtering targets. In order to obtain stoichiometric films, sputtering has to be carried out in the compound mode, which is normally accomplished by low deposition rates and arcing. Moreover, the sensitivity of the deposition process concerning instabilities in the oxygen content of the sputtering gas makes commercial large area applications very difficult [1]. Within this study ceramic sputtering targets of Niobium-, Tantalum- and Tungsten oxide were used to obtain stoichiometric films by DC reactive magnetron sputtering. All target materials were almost fully compacted (density>99%) and showed specific electrical resistivities in the range of 1,0E+02 Ω-cm to 1,0E-04 Ω-cm. During deposition, the process turned out to be very stable regarding oxygen variations in the sputtering gas and arcing was never observed. Compared to reactive sputtering of metallic targets, the deposition rates were significantly higher. The thin films which were obtained show excellent optical properties.

INTRODUCTION

The deposition of dielectric thin films by magnetron sputtering is frequently used in the field of the optical coating industry. Today two distinct sputtering techniques are applied, namely DC reactive sputtering of elemental, metallic sputtering targets and RF quasireactive sputtering of compound, ceramic sputtering targets. The terms “reactive” and “quasireactive” are, thereby, referring to the amount of reactive gas which has to be contained in the sputtering gas in order to obtain stoichiometric films [1]. Within this text, “quasireactive” is used for deposition processes in which the content of reactive gas (O_2) in the sputtering gas (Ar) is < 20 vol%.

In the case of reactive sputtering of elemental targets concentrations of up to 60 vol% of reactive gas are essential. This leads to several difficulties such as poisoning of the target surfaces, which in turn causes arcing and low deposition rates [2, 3]. In addition the sensitivity of the deposition process concerning instabilities in the oxygen content of the sputtering gas makes the deposition of uniform films very difficult [1].

When the sputtering target consists of the compound material to be deposited, much lower concentrations of reactive gas (typically lower than 10 vol%) are sufficient to compensate for the loss of the gaseous constituent which is depleted during the transport and condensation/reaction process [1]. Currently, ceramic sputtering targets are made from the stoichiometric compounds and show low electrical and thermal conductivity. Therefore, only RF sputtering is applicable with the disadvantage that spalling/cracking of the targets frequently occurs during operation.

Recent attempts to optimize the deposition processes have mainly concentrated on the improvement of reactive sputtering. The problem of arcing has successfully been tackled by the introduction of arc suppressor interfaces for DC sputtering and the invention of twin magnetron cathodes [3] which are suitable for AC (MF) sputtering. Plasma control units such as plasma emission monitors (PEM) or lambda probes for closed loop process control have contributed to the stabilization of the process. Despite all improvements the difficulty in controling uniformity of the films has limited the applicability of reactive sputtering especially in the field of large area coating (LAC).

An alternative approach is the improvement of quasireactive sputtering. As stated above, the main disadvantage of ceramic sputtering targets exists in their low electrical and thermal conductivity. However, it is well known that free charge carriers can be generated in transition metal oxides by reduction [4]. The removal of oxygen from the stoichiometric compounds causes the formation of substiochiometric phases, which, in some cases, even show metallic conductivity [5]. Asahi Glass Co Ltd. [6] and Vanderstraeten [7] produced sputtering targets consisting of substoichiometric oxides of several transition metals by plasma spraying and published promising results of deposition experiments which were carried out by quasireactive DC magnetron sputtering. An important advantage of plasma spraying is that parts even with complex shapes like rotatable sputtering targets can be manufactured quite comfortably. On the other hand, plasma sprayed materials often show chemically heterogeneous microstruc-

tures and micropores, which can act as sources of arcs and particle emission during sputtering and thus deteriorate the properties of the deposited film.

In order to overcome these problems substoichiometric, chemically homogeneous and nonporous sputtering targets with fine and homogeneous microstructure were manufactured.

EXPERIMENT

Substoichiometric, planar sputtering targets were manufactured by the application of a modified sintering process. The target properties were investigated by a variety of material testing methods:

- pycnometric measurement of the apparent density
- detection of porosity by ultrasonic testing
- imaging of the microstructure by scanning electron microscopy (SEM)
- determination of the chemical composition by thermogravimetry (TG), volumetric absorption of oxygen and X-ray diffraction (XRD)
- four-point probe measurements of the electrical resistivity and the Hall constant
- determination of the heat capacity by differential scanning calorimetry (DSC)
- laser flash (LF) based measurements of the thermal conductivity
- dilatometric (DIL) determination of the thermal expansion

DC magnetron sputtering experiments were carried out in a Leybold Type Z660 coating system equipped with a Leybold PK200 cathode (target dimensions dia 200 x 6 mm) at a target to substrate distance of 62 mm. MF (40kHz) magnetron sputtering experiments were carried out in a Leybold Type Z600 coating system equipped with a Leybold TwinMag PK 190/76 cathode (target dimensions 190 x 76 x 6 mm). The refractive indices of the thin films which were deposited on Silicon wafers and BK 7 glass substrates were determined by ellipsometry and the extinction coefficients were calculated from photometric measurements of transmission losses.

RESULTS AND DISCUSSION

Target Properties

In Table 1 the physical-chemical properties of the substiochiometric sputtering targets are summarized. For comparison, the data of the stoichiometric materials, which were obtained by oxidation of the substoichiometric materials on air, are also shown. The temperature values in the column "stability against air" ($T_{ox.}$) refer to the onset of the oxidation reaction and indicate that the materials are suitable for bonding at even elevated temperatures. A closer look at the specific resistivity reveals that it is directly related to the degree of substoichiometry for all materials. Contrary to the recent literature and published patents, DC magnetron sputtering was possible with the substoichiometric Tantalum oxide sputtering targets although the specific resistivity of the target materials has been higher than 10 Ω-cm. The thermal conductivity and the thermal expansion are generally low and show, with the exception of the Tungsten oxides, no significant differences between the stoichiometric and substoichiometric materials. No cracking or spalling of the targets was observed. This seems to be surprising regarding the low thermal conductivity of the materials. However, since the thermal expansion of the materials is also low, thermomechanical stress, which evolves during the heat cycles caused by operation, is limited. The comparably high thermal conductivity of $WO_{2,72}$ can be explained by the high density of electrons in the conduction band, which could be detected by ultraviolet photoemission

Table 1: Physical–chemical properties of ceramic sputtering targets

Material	Density ρ [g*cm^{-3}]	Specific Resistivity $\rho_{spec.}$ [Ω-cm]	Thermal Conductivity λ [W*m^{-1}*K^{-1}]		Coefficient of Thermal Expansion CTE [K^{-1}]*10^{6}		Stability against air $T_{ox.}$ [°C]
			25°C	400°C	25°C	400°C	
$Nb_2O_{4,98}$	**4,55**	**3,4E-02**	**2,4**	1,8	**1,6**	1,8	**600**
$Nb_2O_{5,00}$	**4,24**	**> 1E+06**	**2,5**	2,0	**0,6**	1,6	**-**
$Ta_2O_{4,9}$	**8,75**	**7,9E+01**	**1,6**	1,8	**2,5**	2,2	**650**
$Ta_2O_{4,5}$	**9,05**	**5,6E+01**	**1,8**	2,3	**4,8**	2,8	**600**
$Ta_2O_{5,0}$	**8,40**	**> 1E+06**	**1,2**	1,8	**4,2**	2,5	**-**
$WO_{2,72}$	**7,75**	**1,0E-04**	**12,0**	9,0	**2,0**	1,8	**750**
$WO_{2,90}$	**7,12**	**2,5E-03**	**2,9**	4,2	**3,3**	0,1	**600**
$WO_{3,00}$	**6,95**	**> 1E+06**	**3,2**	2,4	**10,0**	16,5	**-**
$ZrO_{1,75}$	**5,60**	**3,4E+00**	**-**	-	**-**	-	**-**

spectroscopy (UPS) and measurements of the Hall constant [8]. The results of these investigations will be discussed elsewhere [9].

All target materials were almost fully compacted (apparent density higher to or equal 99% of theoretical density) and the ceramic sheets were pore free with uniform density distribution. Figure 1 shows the image of a fracture surface of a substoichiometric Niobium oxide ($Nb_2O_{4,98}$) sputtering target as obtained by scanning electron microscopy (SEM). The microstructure is homogeneous in morphology with an average grain size of lower than 10 µm.

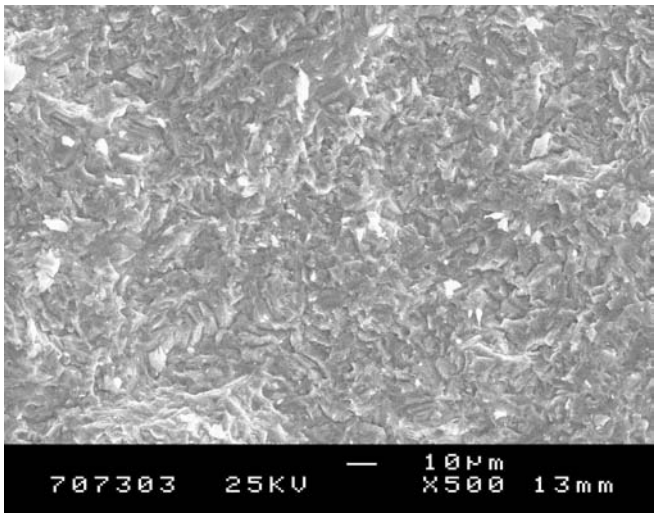

Figure 1: SEM image of the fracture surface of a $Nb_2O_{4,98}$ sputtering target

DC Magnetron Sputtering Experiments

Figure 2 shows the dependence of the total pressure in the coating chamber on the Oxygen (O_2) flow rate during DC magnetron sputtering for a ceramic sputtering target ($Nb_2O_{4,98}$) in comparison to a elemental Niobium target (Nb-met.). For the elemental target the well known hysteresis effect can be observed between increasing and decreasing O_2 flow rates. This behavior is mainly due to the reaction of oxygen with the target surface, which leads to the formation of a passivating oxide layer ("target poisoning"). In the case of the ceramic target, the values are lying on the same straight line for both increasing and decreasing O_2 flow rates. This might be due to the fact that the substoichiometric materials are almost saturated with Oxygen; i.e., compared to metallic targets the affinity of the surface atoms to Oxygen is extremely reduced.

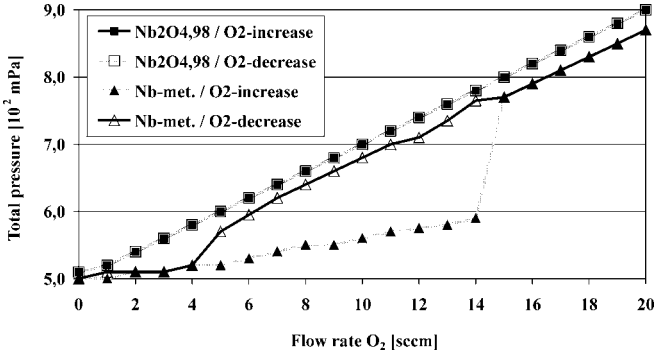

Figure 2: Total pressure versus Oxygen flow rate during DC magnetron sputtering at constant pumping speed and constant Ar flow rate (20 sccm)

It is also well known that the poisoning of metallic sputtering targets results in a drastic decrease of deposition rate. Figure 3 shows the deposition rate as a function of the oxygen (O_2) content of the sputtering gas during DC magnetron sputtering at two distinct cathode power levels (3,34 W/cm^2 and 6,67 W/cm^2) for several ceramic sputtering targets ($Nb_2O_{4,98}$/$Ta_2O_{4,9}$/$WO_{2,72}$) and an elemental Niobium target (Nb-met.). A sharp step appears in the curve of the metallic target in the region between 40 vol% O_2 and 50 vol% O_2. This area is also described as a "transition area" since the sputtering process changes there from the metallic mode to the compound mode.

In contrast to the metallic target the ceramic targets show smooth curves. The deposition rate is monotonically increasing with decreasing oxygen contents. The dashed lines in the diagram indicate the amount of oxygen which is necessary in order to obtain oxide films with stoichiometric composition. The values for the sputtering targets Nb-met., $Nb_2O_{4,98}$, $WO_{2,72}$ and $Ta_2O_{4,9}$ are 50 vol%O_2, 16,7 vol%O_2, 16,7 vol%O_2 and 5 vol%O_2 respectively.

Significant differences between the metallic Niobium (Nb-met.) and the ceramic Niobium oxide ($Nb_2O_{4,98}$) sputtering targets were also observed by varying the total pressure during DC magnetron sputtering (see Figure 4). For both targets the oxygen content of the sputtering gas was adjusted at values that ensured saturation with oxygen, i.e., deposition of stoichiometric films. In the case of the ceramic target the deposition rate could almost be doubled by decreasing the total pressure from 1,0E+03 to 1,0E+02 mPa whereas the deposition rate almost kept constant for the metallic target.

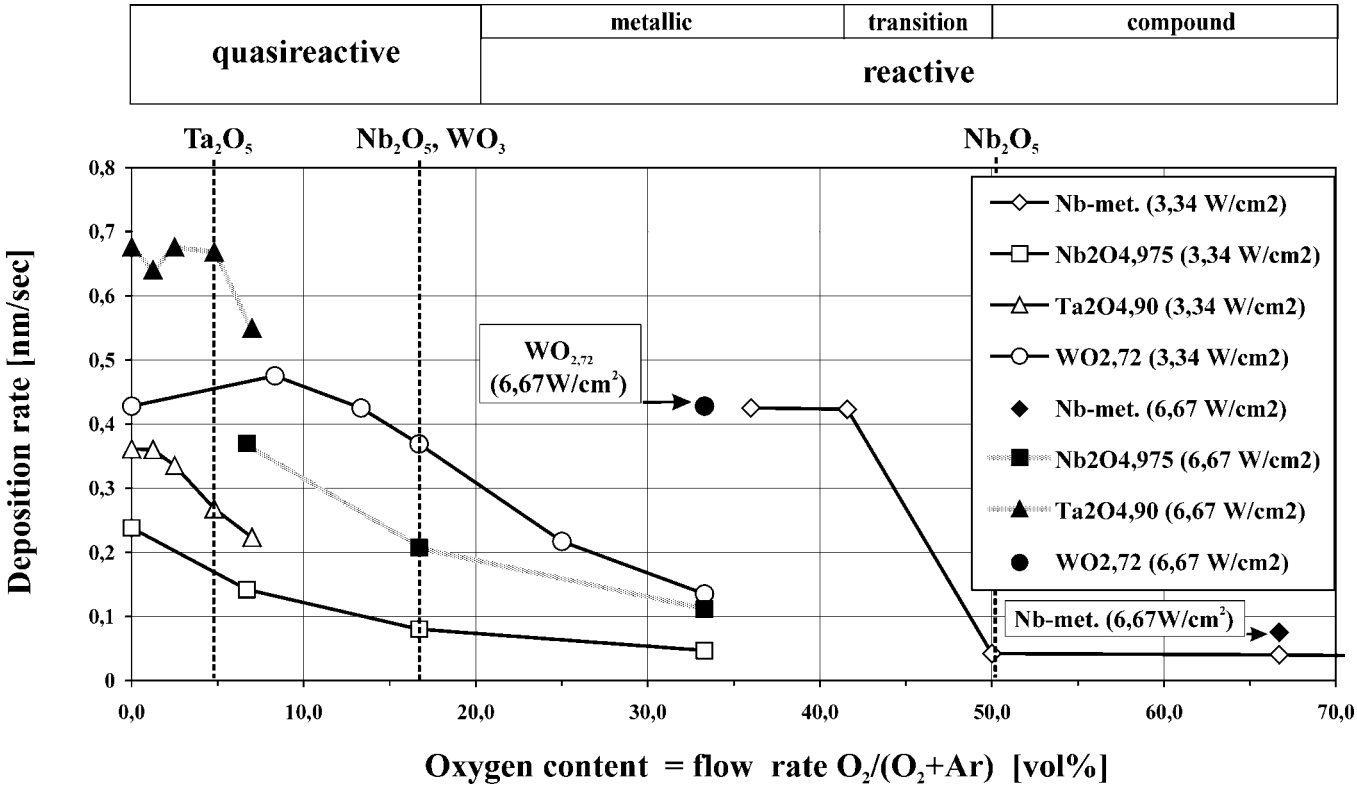

Figure 3: Deposition rate versus Oxygen content during DC magnetron sputtering at constant total pressure ($5*10^2$mPa)

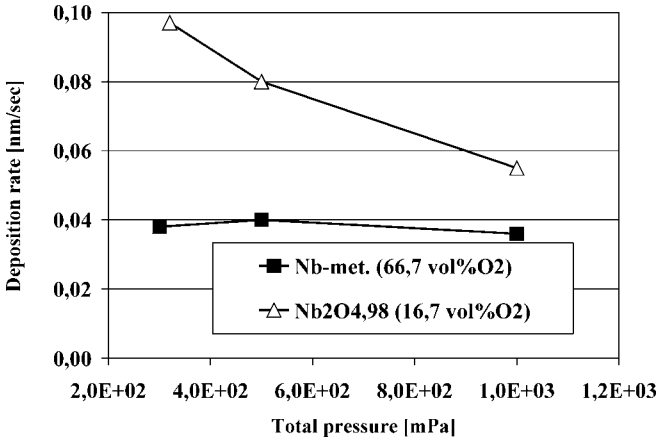

Figure 4: Deposition rate versus total pressure during DC magnetron sputtering

Optical Properties of Thin Films

Dispersion curves were determined for thin films which were obtained by DC quasireactive sputtering of ceramic sputtering targets ($Nb_2O_{4,98}$/$Ta_2O_{4,9}$/$WO_{2,72}$) and for comparison by DC reactive sputtering of a metallic Niobium (Nb-met.) target. Figure 5 shows the refractive indices of thin films with an average geometrical thickness of approximately 250 nm. The values at 550 nm for Nb_2O_5, Ta_2O_5 and WO_3 are 2,34, 2,18 and 2,37, respectively. No significant difference exists between the reactively and quasireactively deposited films.

Contrary to the refractive indices, variations between thin films obtained by sputtering of either metallic or ceramic targets were observable regarding the extinction coefficients. Figure 6 shows the extinction coefficients for Nb_2O_5 films with a geometrical thickness of 4500 nm which were deposited by MF sputtering [10]. The films obtained from the ceramic target show a slightly increased transmittance for radiation with a wavelength higher than 800 nm (IR), whereas the reverse is observable in the region of wavelength between 300 nm and 750 nm (VIS).

SUMMARY AND CONCLUSION

DC/MF quasireactive magnetron sputtering of ceramic sputtering targets is a promising alternative to reactive sputtering of metallic targets for the deposition of dielectric thin films with excellent optical properties. For reactive sputtering the optimum conditions are only achieved at the working point, where it is necessary to control the deposition parameters within very narrow margins. In contrast, the quasireactive sputtering process is characterized by a working area. Within this working area variations of the process parameters do not influence the film properties. This is especially advantageous in large area coating (LAC) applications where it is difficult to obtain a completely homogeneous distribution of the Oxygen within the plasma. Moreover, ceramic sputtering targets are not sensitive to poisoning. Thus, high deposition rates can be achieved for DC/MF magnetron sputtering and arcing does not occur.

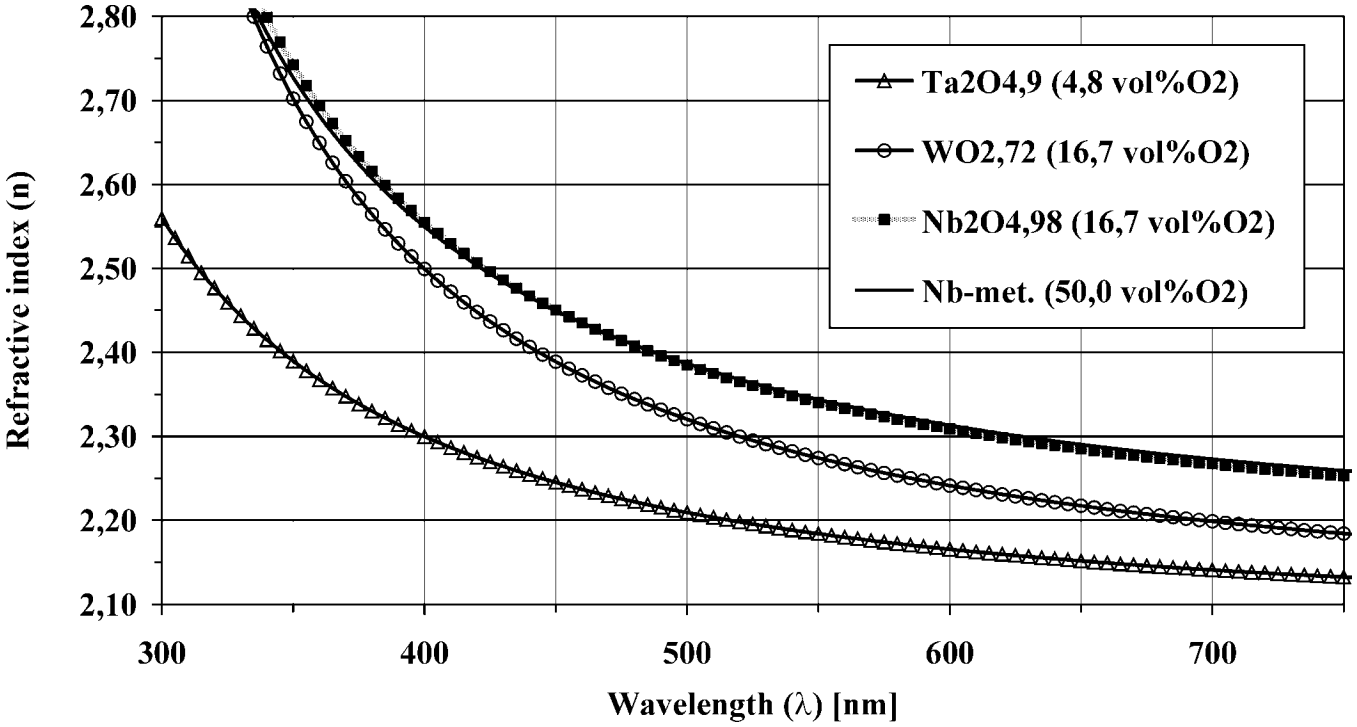

Figure 5: Refractive indices of thin films obtained by DC magnetron sputtering under optimized conditions

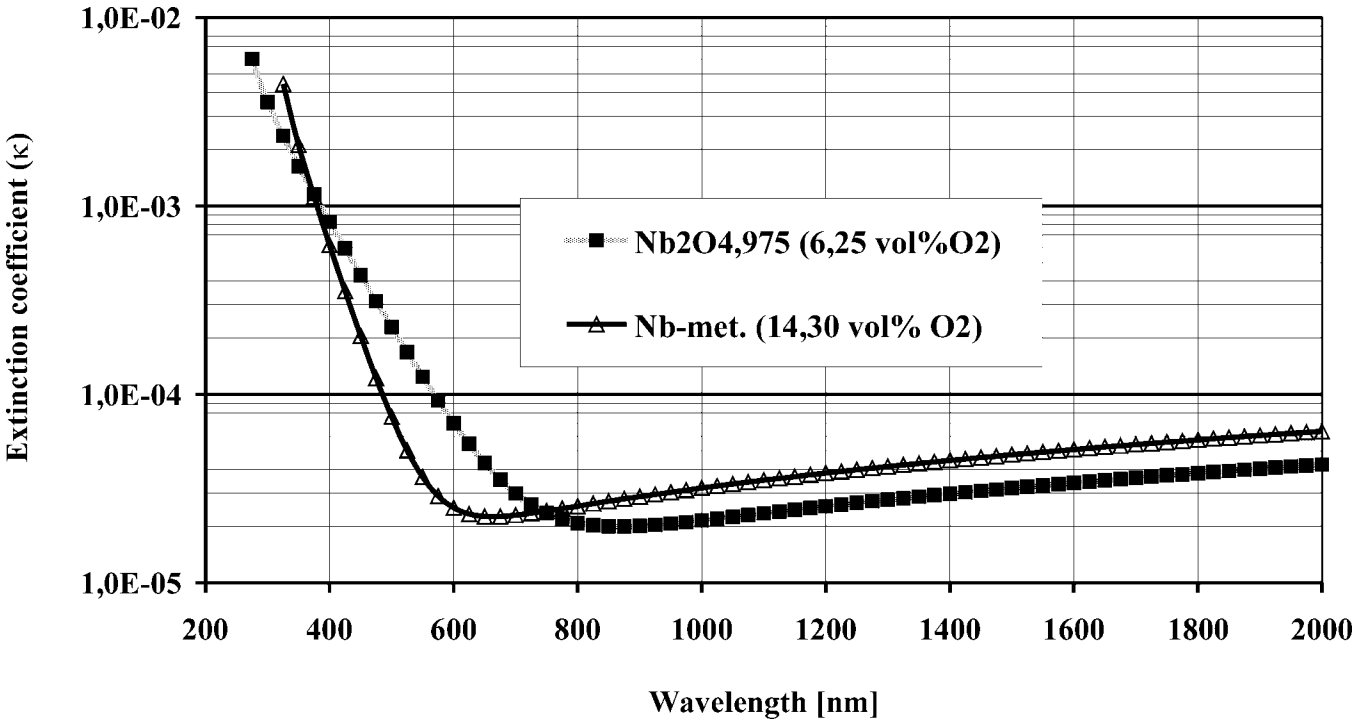

Figure 6: Extinction coefficient of Nb_2O_5 thin films obtained by MF magnetron sputtering under optimized conditions

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