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Preparation and properties of high refractive index tantalum pentoxide coatings deposited by plasma ion assisted deposition with xenon or argon assistance

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Tantalum pentoxide films have been prepared by plasma ion assisted electron beam evaporation, utilizing argon or xenon as the working gases. The optical constants of the layers have been investigated by spectrophotometry, while X-ray reflection measurements and energy dispersive X-ray spectroscopy have been performed to get information about the density and noble gas content of the layers. The correlation between the level of plasma ion assistance and the layer properties is discussed. With respect to optical quality, the application of xenon as the working gas results in coatings with higher refractive index than the application of argon. This effect is attributed to a more efficient momentum transfer from high energetic working gas ions or atoms to tantalum atoms during deposition.

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1. Introduction

1.1. Motivation

Tantalum pentoxide is a standard high refractive index material for design and manufacture of optical coatings with challenging specifications in the near infrared and visible spectral range as well as adjacent ultraviolet spectral regions. It can be prepared by a multiplicity of deposition techniques, including ion assisted deposition IAD [1], reactive ion plating IP [2], ion beam sputtering IBS [3], pulsed laser deposition [4], chemical vapor deposition [5], reactive magnetron sputtering MS [6], electron beam evaporation EBE [7], dip- and spincoating [8] as well as plasma ion assisted electron beam evaporation PIAD [9]. Combined with a low index material such as silicon dioxide, it is in extensive use in numerous multilayer designs [10–12].

In agreement with the general principles of thin film optics, a high index contrast between the high- and low index materials in a coating design is advantageous for fitting sophisticated spectral targets, and therefore, there is a need in techniques that provide high index tantalum pentoxide layers for use in multilayer designs. According to our literature study, the highest refractive indices have been reported for tantalum pentoxide layers prepared by IP methods so far [13].

It is worth mentioning in this context, that starting from the pioneering work [14] of our recently deceased colleague and teacher Prof. H.K. Pulker, IP techniques have been established as a favorite deposition method for oxide optical coatings in cases when absolute priority is placed on highest film density and refractive index [13,15].

With respect to refractive indices, the IP produced coatings are followed by sputtered samples (IBS [3], MS [6]). In this context, the present article is focused on the *potential of PIAD processes* to deliver high index tantalum pentoxide coatings.

In particular, the present study has been triggered by several publications which demonstrated an increase in the refractive index of IAD or PIAD hafnium dioxide coatings when xenon has been used as an inert gas instead of argon (which is the standard choice for the inert gas when operating ion or plasma sources in these deposition processes) [16–18]. The usual explanation is the relevance of momentum transfer processes during film growth [19,20]; once the atomic mass number of xenon (131.30) is closer to that of hafnium (178.49) than that of argon is (39.95), momentum transfer processes are expected to be more efficient when argon is replaced by xenon. If so, one should expect that similar effects will be observed for PIAD deposition of tantalum pentoxide, because the mass number of tantalum (180.95) is quite close to that of hafnium. It was therefore our intention to compare the properties of PIAD tantalum pentoxide coatings, prepared with different working gases, but in otherwise identical conditions.

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1.2. Quantification of assistance effects in this study

Several attempts are known from the literature to quantify the effects of ion or plasma ion assistance on the layer properties in terms of a single parameter that is defined as a conglomerate of experimentally accessible data [19,20]. Such a definition will of course depend on the deposition technique and the in-line process characterization available. Thus, Targove and Macleod [19] studied an IAD process and quantified the assistance effect in terms of a product of incident ion current density, the square root of the incident particle energy, and an atomic-mass-dependent factor to account for the efficiency of momentum transfer processes. In contrast, Kennedy et al. [20] quantified IAD assistance effects in terms of a parameter called energy per molecule. This quantity is calculated by the product of the anode voltage, the anode current and the reciprocal of the evaporation rate (because of the proportionality of the anode voltage/current with the ion energy/density). Unfortunately, for a PIAD process, the thus defined versions of an assistance parameter cannot be applied directly as it will be discussed later.

In view of these studies and further work published on modeling the impact of high energetic particles on the relevant properties of a growing film [21], a suitable combination of at least the bias voltage U_{bias} (which defines the mean kinetic ion energy) and the deposition rate seems reasonable for the definition of an assistance parameter when using PIAD. With respect to the work of Davis [21], the net densification effect under high energetic particle bombardment is observed as a balance between the competing effects of atomic knock-on implantations and particle migration to the film surface activated by thermal spikes (Fig. 1). According to [21], this can be described by Eq. (1) (symbols changed with respect to the original work):

$$\frac{\Delta N}{N_0} \propto \frac{E^{\frac{1}{2}}}{\frac{r}{j} + a\left(\frac{E}{E_{char}}\right)^{\frac{5}{3}}} \tag{1}$$

with E – ion energy, E_{char} – a characteristic energy value, a – a parameter, r – film growth rate, j – high energetic particle flux density, N_0 – bulk atomic density and ΔN – atomic density increase as caused by the assistance during growth.

A characteristic feature of the dependence described by relation (1) is in the strong increase in densification with increasing ion energy, as long as the latter is small enough for neglecting the second term in the denominator in the right-hand term of (1). In this energy region, knock-on implantation is the dominant effect, and the densification is given by:

$$\frac{\Delta N}{N_0} \propto j\frac{E^{\frac{1}{2}}}{r} \tag{2}$$

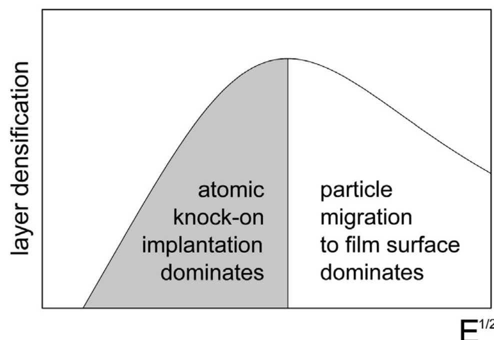

Fig. 1. Influence of the ion energy of bombarding particles to the densification of a growing layer and dominating effects according to [21].

Fortunately, the parameters entering into (2) are partially accessible in a real PIAD deposition experiment: The ion (or high energetic particle) kinetic energy is roughly controlled by the bias voltage U_{bias} [22], and at least the average growth rate may be accurately determined from the process duration and the thickness of the film. So the effects of assistance can, in principle, be studied when changing the bias voltage only, while trying to keep the deposition rate fixed. In contrast to the mentioned IAD experiments [19,20], in PIAD the situation is more complicated with the flux of high energy particles: It is composed from contributions of ions and neutrals [23], and is difficult to be measured practically during a real deposition process. It is therefore hardly quantified. For simplicity we assume, that it is constant in all experiments carried out with the same working gas. Then, within an experimental series where only the bias voltage is intentionally varied, it makes sense to quantify the assistance effect primarily caused by knock-on implantation by a parameter that is proportional to the square root of the bias voltage, being at the same time proportional to the momentum of incident high energy particles. In order to consider possible drifts in the deposition rate, we introduce a dimensionless assistance parameter A therefore according to the definition:

$$A \equiv \frac{(U_{bias}/\mathrm{V})^{\frac{1}{2}}}{r/(\mathrm{nm\,s^{-1}})} \propto \frac{E^{\frac{1}{2}}}{r} \tag{3}$$

For a bias voltage of 100 V, and a growth rate of 0.2 nm s^{-1}, that assistance parameter will be equal to 50, while it is close to zero in the case that no assistance is provided during film growth. Practically, the assistance parameter as defined by Eq. (3) is a compromise between those defined in [19] and [20].

At higher particle energies E, thermal spike effects become more significant, and then Eq. (1) describes a more complicated behavior of the densification on the particle energy: The densification will reach a maximum and then drop down (Fig. 1).

We notice that Eq. (1) does not comply with effects of local density fluctuations (for example pores) and incorporation of contamination (e.g. noble gas atoms) into the network. The particular impact of porosity is considered in subsequent theoretical and experimental work (see for example [24–26]), but no ready-to-use recipe seems available that would allow to give a quantitative prediction of the impact of atomic network densification, porosity and impurity incorporation *in combination* on relevant film properties such as refractive index or film stress.

2. Experimental details

2.1. Layer preparation

All depositions were performed in a Leybold Syrus pro 1100 deposition plant using a HPE6 electron beam evaporator. The substrate temperature was 100 °C ± 1 °C and the oxygen flow was 15 sccm in all experiments. Approximate layer thickness and deposition rate control (0.2 nm s^{-1} target value) during deposition have been accomplished by the QW/TW12 quartz crystal monitoring system using an average tooling factor for all assistance levels. During deposition the layers were densified using an Advanced Plasma Source (Leybold APS pro [22]). The APS was operated in $U_{bias} - I_c$ -control mode (U_{bias} -voltage between floating anode and ground, I_c -magnetic field coil current) and discharge current of the plasma source was fixed to 55 A. In Table 1 the main process parameters are summarized.

In order to eliminate residual errors caused by the dependence of the tooling factor on the assistance, the correct layer thickness has been determined after deposition by means of ex situ spectrophotometry (see Section 2.2). For calculating the actual value of the assistance parameter A, in Eq. (3) we therefore replaced the target value of the deposition rate r by an average deposition rate $\langle r \rangle$ obtained from the physical film thickness d as obtained from spectral

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