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Thickness microscopy based on photothermal radiometry for the measurement of thin films

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ABSTRACT

The photothermal detection technique is an innovative and non-contact method to investigate the properties of films on workpieces. This paper describes a novel experimental set-up for thickness microscopy based on photothermal radiometry. The correlation between the thermal wave signal and the film thickness is deduced and evaluated to determine the film thickness with a lateral resolution of less than 1 mm. Results indicate that the thickness microscopy is a useful method to characterize thin films and has the potential to be applied in-process.

1. Introduction

Generally, thin films are deposited on workpieces to improve properties like wear resistance, hardness, optical transmission and many more. Numerous methods exist to deposit thin films, for instance plasma spray, physical (PVD) and chemical vapor deposition (CVD), and the sol–gel method. The latter is a popular technique with many advantages: No vacuum is required, objects of almost unrestricted size and shape can be coated and, in many cases, sintering at moderate temperatures ($T \leq 300\,^{\circ}\mathrm{C}$) is sufficient. Zirconia oxide (ZrO_2) layers, which can be deposited by the sol–gel technique, are often used to protect metals against heat, wear and corrosion [1]. As an active research field, the preparation and characterization of ZrO_2 films is still of great interest and therefore a matter of current investigation [2].

As it is well known, coating properties, like thickness, microstructure, stress, adhesion to the substrate, hardness and others, determine the quality of the product and require precise measuring methods. The layer thickness, for instance, can be determined by direct methods, which often implies a contacting and destructive procedure [3]. Several non-contact and non-destructive methods exist, usually applicable only to certain types of coatings [4–6]: Optical interferometry and optical ellipsometry measure optically transparent films, eddy current and resistivity can be used for metallic films, beta backscatter and X-ray fluorescence are convenient for certain metallic and other optically opaque films. Unfortunately, there is still no effective and simple non-destructive method to measure thickness of coated films.

Photothermal radiometry, based on temperature phase measurements, can be used for the detection of film thickness. In this method, heat is generated by the absorption of an intensity-modulated laser beam by the film. It can be applied for both optically opaque and transparent layers [7], if the thermal properties of the layer are different from those of the substrate. Two of the methods applicable for the analysis of thermal waves are the infrared detection and the beam deflection. So far, the photothermal radiometry for the thickness detection of zirconia oxide film has not been reported.

In this paper, ZrO_2 films were prepared using the sol–gel method. A thickness microscopy based on photothermal radiometry was built and applied for the experiments described herein. Furthermore, this set-up was used to measure ZrO_2 films thickness and deduced the correlation between the thermal wave signal and the film thickness.

2. Experiments

2.1. Preparation of ZrO_2 film

Polished aluminum disks were used as substrate (thickness = 9 mm, diameter = 50 mm). The main components

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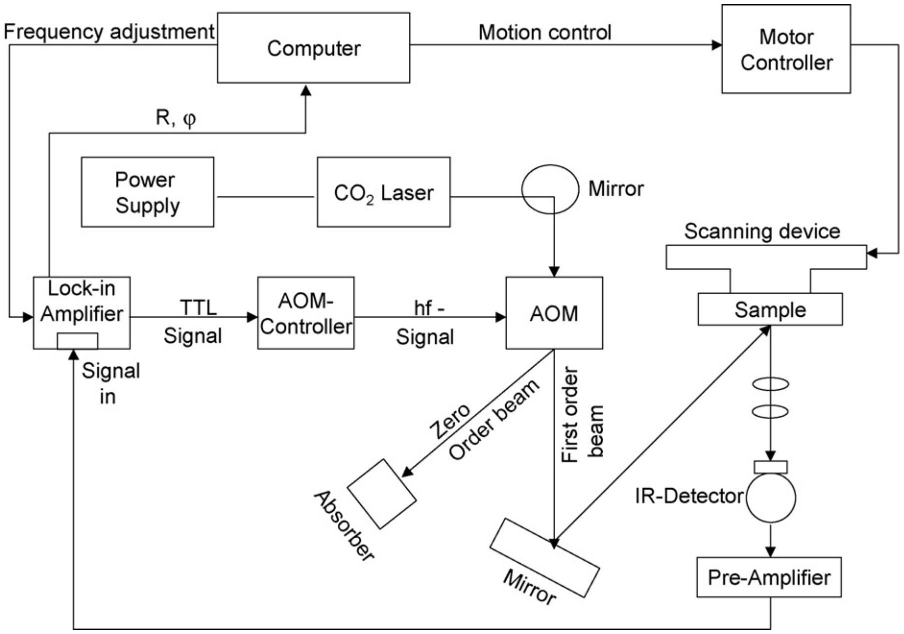

Fig. 1. Sketch of the experimental set-up.

of the sol were tetraethoxysilan (TEOS 99.999%, Aldrich), methacryloxypropyl-trimethoxysilance (MATMS. 98%, Aldrich), zirconium (IV) tetrapropoxide (ZPT), 1-propanol, methacylic acid and water with some drops of HCl. The sol was deposited by spin coating. Varying the rotational speed from 1000 to 2500 rpm formed colorless and smooth coatings with different thicknesses. Then, the wet coatings were dried at 100 °C for 24 h. Reference values of the film thicknesses were measured destructively using the ball cratering method (ENV 1071-2) in order to calibrate photothermal measurements.

2.2. Experimental set-up

Fig. 1 illustrates the set-up for the thickness microscopy, based on photothermal radiometry. A CO_2 laser (output power = 10 W cw, wavelength = 10.6 μm, made by Synrad, Inc.) was used as excitation source. An acousto-optical modulator (AOM, type AA.MG40/A6, made by Opto-Electronique, France) modulated the intensity of the laser beam. The laser beam of about 3 mm diameter generated an average heating power of about 800 mW on the sample surface. An InSb infrared detector (type J10D-M204-R100U-20, from Judson Technologies, LLC, USA), combined with an IR optical system consisting of CaF_2 lenses and a germanium cut-on filter, detected the thermal waves. This arrangement was capable to detect thermal waves with a lateral resolution of about 150 μm. A DSP lock-in amplifier (SR850, Stanford Research Systems, Inc.) was used to filter the weak signal and to analyze its phase lag relative to the modulated heating laser beam.

3. Results and discussion

In photothermal radiometry, heat is generated by the interaction between an intensity-modulated light beam and an extended, three-dimensional sample. Absorption and subsequent deexcitation–relaxation produce heat energy, which propagates into the sample, forming a strongly damped thermal wave. The thermal wave causes the emission of modulated infrared radiation, which is detected by an infrared sensor. The detector signals imply information about the coating properties, such as microstructure, thickness, thermal material parameters, and coating defects.

The solutions of the thermal diffusion equation (TDE) Eq. (1) describe the heat diffusion process, i.e. the temperature distribution $T(x, t)$ with its spatial and time dependency, due to a thermal load $Q(x, t)$ (from the exciting laser beam)

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\kappa(x)\frac{\mathrm{d}}{\mathrm{d}x}T(x,t)\right)-\rho(x)c(x)\frac{\mathrm{d}}{\mathrm{d}t}T(x,t)=Q(x,t) \qquad (1)$$

For a periodic excitation with a certain modulation frequency, thermal waves propagate within the sample. Their penetration depth is given by the thermal diffusion length μ, which, according to Eq. (2), depends on the thermal parameters of the sample and is inversely proportional to the square root of the exciting frequency f

$$\mu=\sqrt{\frac{2\alpha}{\omega}}=\sqrt{\frac{2\alpha}{\omega_0}}\sqrt{\frac{\omega_0}{\omega}}=\mu_0\sqrt{\frac{f_0}{f}} \qquad (2)$$

with the thermal diffusivity $\alpha=\kappa/\rho c$ and $\omega=2\pi f$ (thermal conductivity κ, specific heat c and mass density ρ). μ_0 is the thermal diffusion length at $f_0 = 1$ Hz.

In physical terms, μ is that propagation distance of the thermal wave, after which its amplitude is damped by a factor of 1/e.

If the excitation laser beam covers a large area compared to the thermal diffusion length μ, the TDE is reduced to a one-dimensional equation. It requires an opaque sample, which means that the optical penetration depth must be much smaller than the thermal diffusion length μ. For this constellation, the amplitude of the temperature oscillation directly at the surface of a layered material is given by [8]

$$T=\frac{I_0}{2\kappa\sigma}\frac{1+R\ \exp(-2\sigma d)}{1-R\ \exp(-2\sigma d)} \qquad (3)$$

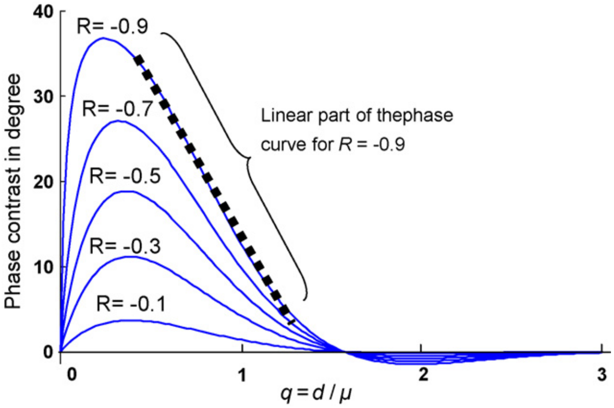

Fig. 2. Phase contrast for different values of the thermal reflection coefficient *R*.

where I_0 denotes the laser intensity, d the layer thickness, κ the thermal conductivity and $\sigma = \mu/(1 + i)$.

R is called the thermal reflection coefficient, which is a real number within the interval [−1, 1] and can be calculated from

$$R = \frac{1 - (e_s/e)}{1 + (e_s/e)} \tag{4}$$

e_s, e_l are the thermal effusivities of the substrate (s) and the layer (l) with

$$e_j = \sqrt{\kappa_j \rho_j c_j} \tag{5}$$

The thermal conductivity κ, the density ρ and the specific heat capacity c are assumed to be constant within layer and substrate and change abruptly at the interface.

Considering that Eq. (3) is complex valued, the photothermal phase signal is given by

$$\varphi = \text{arc}\ \tan\left(\frac{Im(T)}{Re(T)}\right), \tag{6}$$

where Im (T) and Re (T) are the imaginary and the real part of Eq. (3).

Some basic calculation yield

$$\varphi = \text{arc}\ \tan\left(\frac{-1 + R^2\exp(-4q) - 2R\exp(-2q)\sin(2q)}{1 - R^2\exp(-4q) - 2R\exp(-2q)\sin(2q)}\right) \tag{7}$$

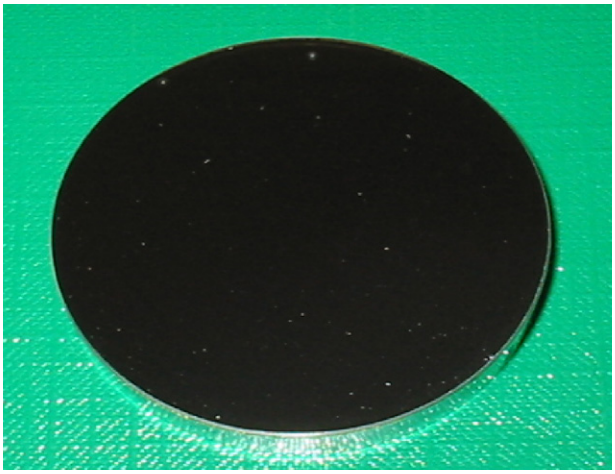

Fig. 3. ZrO_2 coated on the aluminum substrate.

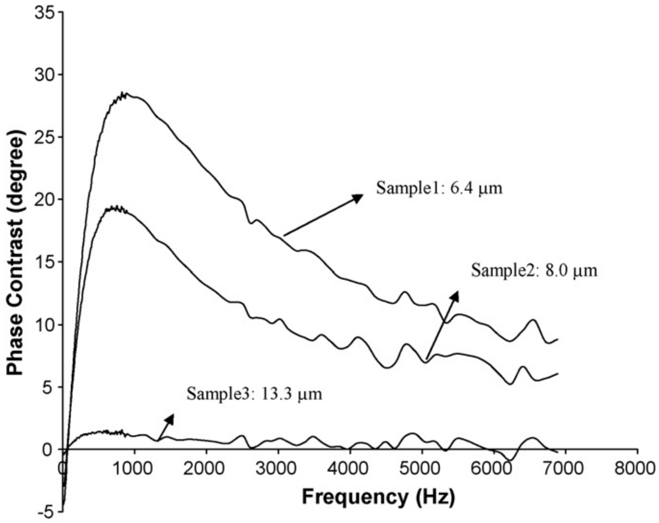

Fig. 4. Phase contrast of the radiometric signal as a function of the modulation frequency.

In this equation, q is the layer thickness, normalized to the thermal diffusion length: $q = d/\mu$.

Fig. 2 shows the function $\varphi(q)$ for different values of R. The thickness interval between the maximum and minimum of the curve is nearly linear and can be used conveniently for layer thickness measurements. Theoretically, a measured phase might be attributed to two different values of the layer thickness. In practise, this problem can be avoided by either evaluating additionally the photothermal amplitude S or by a second phase measurement using a different modulation frequency.

Elaborating a calibration curve by Eq. (3) requires the precise knowledge of the thermal properties for the involved materials. If layer and substrate are not opaque, then the photothermal model must be extended considerably. For instance, in layers which do not absorb the excitation energy directly at the surface, the thermal wave will be generated within the whole layer, maybe additionally within the substrate. Depending on the reflectivity of the interfaces (layer–gas, layer–substrate), optical interference effects must be taken into account. As the infrared signal will be generated not only from the layer surface, contributions from the whole layer volume must be summed up. The chance to find all the required input data for such an extended photothermal model is low, hence, it will be the easiest and most reliable way to elaborate a calibration curve by measurements.

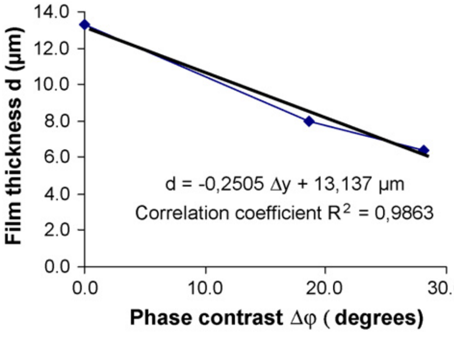

Fig. 5. Phase contrast as a function of the film thickness at 1 kHz.

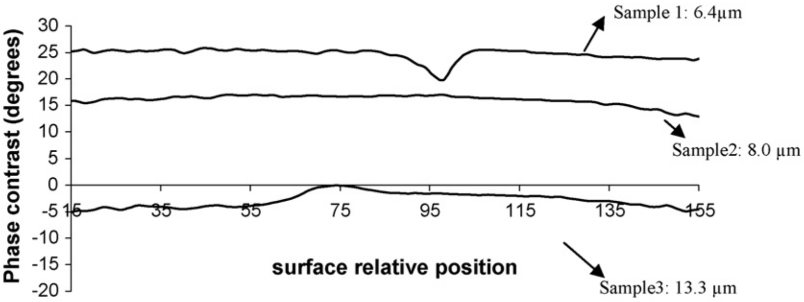

Fig. 6. Phase shift measured at $f = 1$ kHz while scanning the sample surface from 0 mm to 50 mm.

For a non-homogeneous sample like the ZrO_2 coated samples in this research, the resulting temperature distribution and the measured surface temperature (amplitude S and phase φ) depend on the two combined materials, the ZrO_2 coated film thickness and any possible thermal contact resistance in between. For a photothermal characterization of unknown objects, the sample properties have to be extracted and calculated from the measured data.

In order to eliminate the influence from the electronic devices, the two photothermal signals (amplitude S and phase φ) are usually normalized to values measured at a sufficiently thick surface layer, where, due to the damping of the thermal waves, no thermal interference effect occurs. This yields the so-called "contrast curves". The amplitude and phase signals, which correlate with material properties, are derived from the temperature signal $T(t)$ by the lock-in technique. While the amplitude signal is influenced by variations of the laser power and the working distance, the phase signal is essentially independent of these parameters. Therefore, only the phase contrast curves are presented in the following graphs.

Three ZrO_2 coated samples with thicknesses of 6.4 μm, 8.0 μm and 13.3 μm were studied. Fig. 3 shows one of the ZrO_2 coated samples. As shown in the figure, the surfaces of the ZrO_2 coated samples were smooth visually. The phase contrast $\Delta\varphi = \varphi_{\text{ref}}(f) - \varphi_{\text{sample}}(f)$ was calculated by subtracting the phase of the examined sample from the measured phase of a reference sample. Fig. 4 shows the measured phase contrast as a function of the modulating frequency. As it is difficult to produce sufficiently thick ZrO_2 layers by the sol–gel method, the phase values measured at the thickest layer (thickness $d = 13.3$ μm) were taken as reference. The noise of the phase contrast was about 2°. The results indicate that the photothermal phase signal measured for ZrO_2 coatings is highly sensitive, yielding contrast values of almost 30° at $f = 1$ kHz and a signal/noise ratio of more than 10.

A calibration curve was derived from the phase contrast curves at 1 kHz (Fig. 5). Obviously, the phase contrast linearly depends on the layer thickness d within the examined range of thickness.

Fig. 6 shows the results of phase measurements at different positions and at a constant modulating frequency of 1 kHz, Fig. 7 reflects the corresponding layer thicknesses, calculated using the mentioned calibration function (Fig. 5). The surface scanning was carried out from one sample edge to the opposite edge. Obviously, the sample with ZrO_2 thickness of 8.0 μm was coated homogeneously, whereas the sample with a coating thickness of 13.3 μm shows a variation. It is assumed that this was induced by handling the sample shortly after the spin coating procedure. The surface scan of the sample with a coating thickness of 6.4 μm shows a sharp peak (Figs. 6 and 7). In this case there was a defect on the coating, probably caused by dust or impurities of the sol. The estimated defect size was less than 7.0 mm.

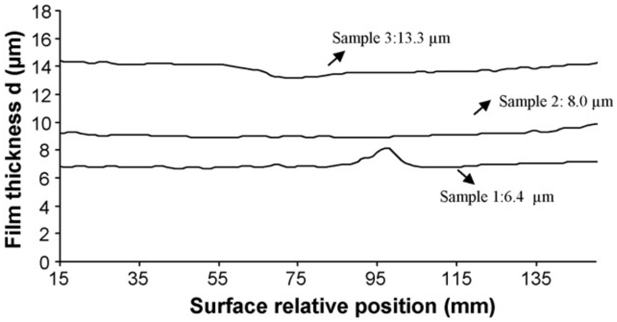

Fig. 7. Thickness microscopy on the sample surface from 0 mm to 50 mm.

At a modulation frequency of $f = 1$ Hz, the thermal diffusion length of metals and semiconductors will be in a range of 2–4 mm, whereas for most dielectric materials, μ ($f = 1$ Hz) will be about 200 μm. Considering the frequency dependence of Eq. (2), the thermal diffusion length of the layer will be about 6 μm at the chosen frequency of $f = 1000$ Hz. This means that the lateral resolution will be limited essentially by the size of the infrared sensor element and not by the thermal diffusion length.

4. Conclusion

According to the results shown above, the photothermal set-up can be used to measure the thickness of ZrO_2 layers. Scanning the surface revealed the size and position of a coating defect. This is helpful to study the quality of thin films and to improve the procedure of preparation. In contrast to other methods of thickness measurement, the photothermal techniques offer a near-process or an in-process inspection in industrial environments.

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