A Facile Method for the Density Determination of Ceramic Thin Films Using X-ray Reflectivity

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**Abstract**

A fast and non-destructive method based on X-ray reflectivity was developed to determine the density of sol-gel derived ceramic thin films, without prior assumptions on the microstructure of the system. The thin film density is calculated from the critical angle , *i.e.* the maximum angle at which total external reflection is still observed, which becomes increasingly difficult for imperfect films. We propose a simple numerical approach, instead of laborious fitting procedures, to determine the thin film density. A *pseudo*-critical angle, , was defined by the first minimum in the 3rd derivative of the reflectivity curves. The measured samples were compared with calibration curves obtained from simulations with changing film densities. Although the absolute positions of  and  are different, similar shifts are observed with changing density. The accuracy of the described method was validated by determining the density of single crystal substrates (ρrel = 100%) and by Rutherford backscattering spectroscopy in combination with scanning electron microscopy. Varying sample size, film thickness, and film/interface roughness of yttria-stabilized zirconia films were found to have no influence on the final calculated density.

**Keywords**

Sol-gel, thin film, density, X-ray reflectivity

**1. Introduction**

Material properties of thin films are strongly affected by their microstructure, and for many applications it is crucial to optimize the deposition and thermal treatment conditions to control parameters such as film thickness, crystallinity and orientation, density, and surface roughness. Most of these parameters can be quantified by standard analytical techniques such as scanning and transmission electron microscopy (SEM/TEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). However, the density of thin films is difficult to quantify experimentally. In this paper, we propose a simple and accurate method to determine the film density of ceramic thin films. The method, based on well-established and easily accessible techniques, is demonstrated by the experimental determination of the density of single crystals and polycrystalline thin films. There are several known methods of density determination, each with their own advantages and disadvantages as outlined below, but the method we propose here is applicable to all types of ceramic thin films, and is even suitable for use on a routinely basis by virtue of its simplicity, while it does not require prior knowledge of the microstructure of the system under investigation.

The best known example of density determination is Archimedes’ method. However, it is not applicable to thin films since the volume displacement caused by a film is too small to be accurately determined. More common is to analyze a film cross-section by SEM. The film density can be calculated from the ratio of particles and pores as determined from the local variation in optical contrast. Often, laborious computer procedures are needed [1,2]. The underlying assumption is that the fraction of surface area covered by pores and particles in the 2D cross-section is equivalent to their volume fractions in 3D, which may not always be the case.

An alternative strategy is to determine the film thickness or the mean particle diameter and compare it with the thickness of a fully sintered film or the mean diameter of a fully sintered particle, respectively [3,4]. The difference can be described as the entrapment of pores, and the relative density  is calculated from:

|  |  |  |
| --- | --- | --- |
|  | or | Eq. (1) |

where , , , and  are the thin film thickness of the measured and a fully dense film, and the experimental and theoretical (= dense) mean particle diameter, respectively. This implies that prior knowledge on the densification behavior of the film is necessary. Besides, this technique is also destructive to the sample.

The Swanepoel method is a non-destructive method that can be used to accurately determine (<1% error) both the film thickness and density [5-7]. The calculations are based on the transmittance spectrum of a thin film on an optically transparent substrate. The experiments are simple, but the different models that are needed to fit the data can lead to varying refractive indexes, and thus to varying densities [6]. Moreover, in general the data cannot be extrapolated to other (non-transparent) substrates, since strain caused by differences in thermal expansion coefficients between film and substrate affects the densification behavior of the thin films [8,9].

Rutherford backscattering spectroscopy (RBS) is a common, non-destructive technique for thin film analysis. It is based on the recoil of high energy (1-2 MeV) He2+ ions off a sample’s surface under a well-defined angle, and can be used to obtain information on element stoichiometry and either film thickness or density. Also, it can be used to measure impurities, and for depth profiling. Although nearly all elements of the periodic table (Z > 6) can be detected, it is not equally sensitive for all elements (error 1-5%). Lastly, the relatively high experimental costs prohibits its use as routine analysis technique.

Ellipsometry is another non-destructive optical technique that is often used for thin film analysis. The reflectance of a polarized light beam that irradiates a sample is measured. Optical constants and thin film thickness are determined indirectly by measuring the amplitude and phase difference between two reflected beams. However, only in the simplest case of an infinitely homogenous thick film, the optical constants and film thickness can be determined directly. In all other cases the amplitude and phase difference are calculated *via* iterative modeling procedures. In general, one can accurately determine the density with ellipsometry, but a combination of complex models is necessary to fully describe the investigated sample, since the used parameters have no direct (universal) physical meaning [10].

Another well-established and non-destructive technique for thin film analysis is X-ray reflectivity (XRR); a versatile method that can be used for crystalline, amorphous, and even liquid samples [11,12]. An X-ray beam impinges the thin film surface at a low angle of incidence. Below the critical angle of total reflection, , the surface acts as a mirror, and the beam is totally reflected. At angles larger than , the measured beam intensity rapidly drops and film thickness, roughness, and chemical composition can be obtained by fitting the full reflectivity curve with well-known models [11-13]. The value of the critical angle determined by the curve fit is directly related to the electron density, which is proportional to the average thin film mass density. Although this technique is widely used in thin film analysis of films grown by chemical vapor deposition (CVD) or pulsed laser deposition (PLD), it is not often used in the field of sol-gel and other wet chemistry-derived ceramic thin films [14-16].

An overview of all of the abovementioned techniques is presented in Table 1. We were interested in developing a high throughput, high accuracy method. And although RBS measurements qualify with respect to accuracy, the technique is rather expensive for routine analyses of large numbers of samples. We therefore chose XRR for density determination, since the measurements are fast and easy to perform using standard laboratory diffractometers. The theory behind the models is well-understood, which simplifies data analysis. In general the method assumes an isotropic film, but a density gradient can be taken into account [17].

As was mentioned above, XRR is often used for thin films grown with physical vapor deposition techniques. Since these films are typically stoichiometric and of high density, the reflectivity curves are only partially fitted at angles  to determine the thickness and the interface roughness. Consequently, the calculated densities obtained *via* these partial fits are rather inaccurate and may deviate largely from the real density values. Since the thickness, microstructure, and roughness of sol-gel and other ceramic thin films are usually evaluated during the optimization of the deposition process, e.g. from SEM images on cross sections and AFM, only an accurate determination of the critical angle or inflection point is additionally needed to determine the density of the thin film.

In this paper we describe a simple and quick numerical approach to accurately determine the inflection point of X-ray reflectivity curves. With this method we determined the density of sol-gel derived yttria stabilized zirconia (YSZ) films. The method was validated by measuring the density of sapphire and zinc oxide single crystal substrates (ρtheoretical = 100%) and RBS measurements, and was subsequently extended to thin films deposited on a substrate. It is demonstrated below that film thickness, surface roughness, and choice of substrate have no apparent effect on the final calculated density. The key advantage of our approach is that an often very challenging complete curve fit is not required.

**2. Theory**

**2.1 General**

X-ray reflectivity or reflectometry is an X-ray technique that is based on the scattering effects of smooth surfaces measured at very low angles of incidence. It was first described by Compton in 1923 [18]. He found that the density of metal substrates was related to a so-called critical angle. Due to the low angles of incidence, the penetration depth of the X-rays is low and only structural information of the top surface is obtained, which can be extrapolated for completely homogeneous films. Moreover, below the critical angle, it leads to the phenomenon of total external reflection for smooth films, where the angle of incidence equals the angle of reflectance,  (see Figure 1a). Another surface phenomenon, refraction, is observed when the X-ray beam passes from one medium to another, and is described by Snell-Descartes’ law:

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| --- | --- | --- |
|  |  | Eq. (2) |

where , , , and  are the angles of incidence and refraction, and the refractive indices of media “0” and “1”, respectively. X-ray reflectivity measures the angles with respect to the sample’s surface instead of its normal, therefore, cosines are used. Since the refractive index of air (= ) is 1, the expression can be written as:

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| --- | --- | --- |
|  |  | Eq. (3) |

This technique does not rely on diffraction, and for this reason amorphous films can also be investigated.

**2.2 Refractive Index of X-rays & Critical Angle**

The refractive index of X-rays in media is slightly smaller than unity. The complex refractive index can be described as a deviation from unity with a real dispersive part (associated with density and chemical composition) and an imaginary dissipative part (associated with absorption effects):

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|  |  | Eq. (4) |

Here  and  are the dispersive and dissipative part of the refractive index, respectively, and can be described as:

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| --- | --- | --- |
|  |  | Eq. (5) |
|  |  | Eq. (6) |

where  is the X-ray wavelength (typically 1.5418 Å for Cu Kα),  the classical electron radius (2.818·10-15 m),  the electron density, and  the attenuation coefficient. The latter is related to the material’s density *via* the mass attenuation coefficient  (in cm2/g), and can be found in the International Tables of Crystallography [19]. The dispersive part  has typically values in the range of 10-5 to 10-6, for the dissipative part  the values are approximately an order of magnitude smaller. The deviation from unity caused by the imaginary dissipative part is so small, that it is often neglected, *i.e.* . The expression for the refractive index is then described by:

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| --- | --- | --- |
|  |  | Eq. (7) |

Since the transmittance into the material then equals zero, the relationship, after derivation, between the angle of incidence and the real dispersive part can be written as:

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|  |  | Eq. (8) |

and total external reflection can only be observed under very small angles, when  <  is still valid. The critical angle of total external reflection is thus described by , which usually lies in the range of 0.1-0.4º for Cu Kα irradiation. For materials with known stoichiometry, the mass density of the measured material *ρm* is directly calculated from ρ*e* in Eq. (5):

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| --- | --- | --- |
|  |  | Eq. (9) |

Here  and are the mass and electron density,  Avogadro’s number,  the atomic weight, and  the atomic number. This equation, however, can only be used for mono-atomic materials. For more complex structures such as fluorite or perovskite materials, the mass density may be calculated using the sum of the individual atoms in the unit cell [11].

**2.3 Fresnel Reflectivity**

An X-ray beam can be described as a propagating wave; the magnitude and direction in which the beam propagates is described by wave vectors for the incident, reflected, and transmitted waves. The wave vectors describe the X-ray beam’s behavior when propagating through media with different refractive indices:

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| --- | --- | --- |
|  |  | Eq. (10) |

The Fresnel coefficients, *r*, are calculated for the electric field of the beam perpendicular (s-polarization) and parallel (p-polarization) to the scattering plane. Since the difference between s- and p-polarization is small, it is often neglected. The ratio of total reflected and incident intensity of the measured sample, , is thus the product of the calculated coefficients, see Eq. (10). Here  and  are the vertical components of the wave vectors of the incident and transmitted beam (for the s-polarized electric field), respectively, as shown in Figure 1a.

**2.4 Parratt’s Formalism**

*2.4.1 Homogenous Media of Infinite Thickness*

The reflection of smooth and homogenous media can be calculated by substitution of Snell-Descartes’ law into the Fresnel equations [20]. In view of Eq. (11) and Eq. (12), the ratio of reflected and incident intensity of the beam is only dependent on the critical angle,, and the absorption of X-rays in the medium,.

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| --- | --- | --- |
|  |  | Eq. (11) |
|  |  | Eq. (12) |

Figure 2 shows the calculated reflectivity of a homogeneous medium (bulk) with a smooth top surface at a fixed critical angle of 0.65º, according to the abovementioned formulas. When the sample acts as a perfect mirror, all the incident beam’s energy is reflected below the critical angle and . The critical angle is easily determined as the angle where an abrupt decrease of intensity occurs. With increasing interface imperfection or surface roughness, the absorption of X-rays into the film (and thus ) increases, and a gradual decrease in the beam’s intensity is also observed below the critical angle, *i.e.* . As a result, an abrupt intensity drop at the critical angle does not occur, which makes its experimental determination challenging. Although in absolute terms both  and are dependent on the material’s stoichiometry and density, the ratio  does not change with varying density, see Eq. (5) and (6).

*2.4.2 Thin Film(s) on a Substrate*

In more complex cases than the reflectivity of a substrate or an infinitely thick film, e.g. thin films on a substrate, multilayers, and superlattices, Parratt’s formalism can be used in a recursive manner. The Fresnel coefficients of the individual interfaces (starting from the substrate) are used to calculate the reflectivity according to:

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|  |  | Eq. (13) |

For a thin film on a substrate as depicted in Figure 1b, the Fresnel coefficients are calculated for the film-substrate and air-film interface, from which the total reflected intensity can be calculated:

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|  |  | Eq. (14) |

Here  and  are the Fresnel coefficients of the air-film and film-substrate interface, respectively, and  is the film thickness. The reflected beam intensity is thus reduced by reflection at the separate interfaces and absorption in the individual layers (incorporated in the wave vectors of Eq. 13) [11].

Figure 3 shows simulated reflectivity curves based on Parratt’s recursive formalism, and illustrates the effect of changes in the film density, thickness, and roughness on the shape of the curve. An increase in the film density results in a shift of the complete curve towards higher angles, as shown in Figure 3a. A change in the film thickness results in a phase shift, the cosine term in Eq. (14), and is related to the difference in refractive index between the thin film and the substrate. Oscillations are observed in the reflectivity curve (for ) as a result of this phase shift, and an infinite sequence of reflections is possible, see Figure 1b. These oscillations are known as Kiessig fringes [21], and their periodicity decreases, according to , for increased film thicknesses as shown in Figure 3b. Due to the angle dependence of the penetration depth of the X-ray beam into the film, the oscillations are only observed at incident angles . Whereas at low incident angles the penetration depth is in the order of 1-5 nm (top surface information), the penetration depth increases rapidly to approximately 100-1000 nm around the critical angle. For (ideal) smooth films and interfaces, Fresnel reflectivity is observed and the intensity decreases rapidly according to 1/*Q*4 = (4πλ/sin *θ*)4 [11]. As shown in Figure 3c, a more abrupt intensity drop is observed at increased interface roughness between the substrate and film. Since all surfaces have some degree of roughness, modifications of the Fresnel coefficients for microscopic surface roughness have been described by Névot-Croce [22]:

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|  |  | Eq. (15) |

where  is the root mean square (RMS) value for the roughness,  the surface/interface modified with microscopic roughness, and  the ideal smooth surface/interface, respectively. The Fresnel coefficients for rough film-substrate () and air-film () interfaces can thus be individually calculated and used in Eq. (13) and Eq. (14) to fully describe the investigated system. More information on X-ray reflectivity can be found in books by Birkholz *et al.*[11], Als-Nielsen and McMorrow [12], and Daillant and Gibaud [13].

**3. Experimental Section**

**3.1 Chemicals and Materials**

Zirconium (IV) *n*-propoxide (Zr[(OC3H7)]4), 70 w/w% in propanol) and yttrium (III) nitrate hexahydrate (Y(NO3)3·6H2O, purity 99.9%) were purchased from Alfa Aesar GmbH. Glacial acetic acid (99.8%), 2-methoxyethanol (99.3%) and 1-propanol (99.9%) were acquired from Sigma-Aldrich. All chemicals were used as-received from the suppliers without any further purification. Due to its high reactivity, the zirconium (IV) *n*-propoxide was stored and handled in a water-free environment (< 0.1 ppm H2O).

**3.2 Sol-Gel Precursor Preparation**

A 1.0 mol/dm3 solution of zirconium (IV) *n*-propoxide in 2-methoxyethanol was made in a glove box and stirred for 24 h under nitrogen atmosphere. After addition of glacial acetic acid, the reactants were allowed to mix for 5 min; subsequently, an yttrium (III) nitrate hexahydrate solution in 1-propanol was added, resulting in a final [Zr] = 0.6 mol/dm3. The amount of yttrium (III) was equivalent to 3 mol% Y2O3 to ZrO2, *i.e.* to form 3YSZ. More details on the sol-gel precursor preparation can be found elsewhere [23].

**3.3 Substrate Preparation**

Prior to thin film deposition, single crystal sapphire (10x10x0.5 mm3, () orientation; CrysTec) substrates were cleaned with a jet of pressurized CO2 on a hot plate at 250 ºC and subsequently treated with oxygen plasma (Harrick Plasma, Ithaca, USA) operating at 24 W for 150 s to remove organic residues attached to the surface. The substrates were used directly after this surface treatment. As a reference for a fully dense film (ρrel = 100%), sapphire and zinc oxide single crystal substrates (10x10x0.5 mm3, () and (0001) orientation, respectively; CrysTec) were measured as received.

**3.4 Thin Film Preparation**

Thin films were prepared by spin-coating the sol-gel precursor using a Laurell spin-coater (Model WS-400B-6NPP/LITE/AS/OND). Substrates were held in place using a vacuum stage and the deposition chamber was continuously purged with dry nitrogen gas. All films were obtained by rotating the samples for 40 s at 3000 rpm. Directly after thin film deposition, the samples were placed on a hot plate at 150 ºC, on which they were allowed to dry for 1 h. Subsequently, the samples were annealed for 1 h in a pre-heated microwave oven (MultiFAST, Milestone, Sorisole, Italy) at temperatures ranging from 650-1000 ºC.

**3.5 Thin Film Characterization**

X-ray powder diffraction (Bruker D2 Phaser, Bruker AXS, Karlsruhe, Germany) was used to confirm the formation of the 3YSZ phase. The average film thickness of the samples was determined by high-resolution scanning electron microscopy (HR-SEM, 2.5 keV, Zeiss 1550, Zeiss, Sliedrecht, The Netherlands). To reduce image drift as a result of the non-conducting sapphire substrate, approximately 13 nm of Cr was deposited on the 3YSZ thin film (RF sputtering). Cross-sections of at least 5 different areas were investigated. Atomic force microscopy (AFM; Dimension Icon, Bruker Nano, Santa Barbara, CA, USA) was used to determine the surface roughness of the thin films. Per sample, the RMS surface roughness was determined on three different locations with an area of 5x5 µm2, using the Gwyddion software package (version 2.25). RBS measurements were carried out as a reference method for the density determination by Detect99, Utrecht, The Netherlands. The measurements yielded the individual number of (Y + Zr) and O atoms per cm2 from which the average thin film density could be calculated.

**3.6 X-ray Reflectivity Measurements**

X-ray reflectivity measurements were carried out using a Bruker D8 reflectometer (Bruker AXS, Karlsruhe, Germany). Samples were scanned under very low incident angles using Cu Kα irradiation (λ = 1.5418 nm), from  = 0.4-1.0º (step sizes of 0.001º; 1.5 s per step; 0.2 mm slits) with an acceleration voltage and current of 45 kV and 40 mA, respectively. All samples were measured and re-aligned at least 5 times to determine the average measurement error.

*3.6.1 Sample Alignment*

All samples were aligned and measured according to the following procedure, see Figure 4 for a schematic representation. (1) Prior to starting the measurements, the detector ( axis) was aligned with respect to the direct beam within a 0.001º error margin. (2) Spin-coated samples often show height variation at the edges of the substrate, the x- and y-axis of the sample were therefore aligned at the center of the sample. (3) The sample surface was aligned in the center of the direct beam using a z-axis scan. Subsequently, the maximum intensity in a rocking curve was selected. (4) The sample was aligned below the surface with a second z-axis scan, and subsequently (5) a chi-scan was executed to remove a possible tilt from the sample mounting. (6) Again the sample surface was aligned in the center of the direct beam using a z-axis scan, and finally (7) a second rocking curve was measured (at  = 0.4º), and the maximum peak intensity was selected to correct for sample tilt.

*3.6.2 X-ray Reflectivity Simulations*

Reflectivity curves of thin 3YSZ films on sapphire substrates were simulated using the DIFFRACplus LEPTOS software package (version 7.03). Fitting parameters (Table 2) such as layer thickness and surface roughness were obtained from results of HR-SEM and AFM analyses, respectively. Simulation curves of 3YSZ thin films with different density values, ranging from 5.05 to 6.05 g/cm3, were made. As a reference, reflectivity curves of Al2O3 (ρ = 3.984 g/cm3; RMS roughness 0.150 nm) and ZnO (ρ = 5.655 g/cm3; RMS roughness 0.150 nm) single crystal substrates were simulated.

**4. Results and Discussion**

**4.1 Method for Thin Film Density Determination**

From Figure 2 it is apparent that critical angle determination becomes increasingly difficult for increasingly imperfect films or interfaces (higher  value). Although the critical angle for all simulated reflectivity curves is equal, the  position of the inflection point (where the rapid intensity decrease is observed) changes. In order to accurately determine the density of our sol-gel derived thin films, the following steps were carried out: (1) Reflectivity curves with different layer thickness and surface roughness, representing our real samples, were simulated for different thin film densities. The simulation parameters are shown in Table 2. The results were also compared to simulations with under- and overestimated interface roughness and density, to verify the method’s robustness. (2) A *pseudo*-critical angle (; inflection point) was accurately derived (numerically, see section 4.1.1) from both the measured and simulated reflectivity curves. (3) The thin film density of the measured samples was directly determined by comparing the  position of its *pseudo*-critical angle with a calibration curve obtained *via* the simulations. The calibration curve was obtained by plotting the inflection points ( position) of the simulated reflectivity curves versus its manually changed densities.

*4.1.1 Determination of the pseudo-Critical Angle*

The *pseudo*-critical angle was numerically calculated for the simulated reflectivity curves using the Origin Pro 8.1 software package, by determining the first minimum of the 3rd derivative (see Figure 5). We chose this procedure since it yields a reproducible value very close to the real critical angle while systematic errors between the *pseudo*-critical angle and the real critical angle are cancelled out *via* the calibration curve. The 1st derivative of the intensity is not suitable to determine , since it is located where the steep intensity drop  occurs (see Figure 5b). Changes in sample/interface roughness significantly influence the slope in this regime, and thus a correct determination of the position of  is not possible. The simulations are based on the assumption of an infinitely large sample. Thus, no effect of the beam footprint is observed below the critical angle, *i.e.* . For these simulations, the 2nd derivative would be suitable to reliably estimate  (see Figure 5c). However, when small “real” samples are being measured, the intensity increase caused by the beam footprint (most pronounced for sample sizes smaller than approximately 5 cm2 [11]; see Figure 5a) might easily influence the reliability of the determination of the *pseudo-*critical angle. We therefore used the 3rd derivative to get a value for , because its first minimum was not influenced by the size, thin film thickness or roughness of the samples. Significant changes in sample thickness (50-300 nm) and thin film roughness (0.0-2.0 nm), had no significant influence on the position of this experimentally determined *pseudo*-critical angle (see Online Resource 1-3). Thus, the effect of minor deviations within a batch of samples can be neglected.

Because our results are compared with simulations of imperfect films (the real surface/interface roughness of both sample and substrate taken were into account), shifts of the *pseudo*-critical angle can only be caused by changes in the density. The observed shifts are thus equal to the shifts observed for the real critical angle, demonstrating that our method is independent of sample size or roughness, and thus applicable to various thin film deposition techniques.

**4.2 X-ray Reflectivity of Single Crystal Substrates**

Single crystal substrates of sapphire and zinc oxide were used to quantify the accuracy and experimental error of the proposed method. The *pseudo*-critical angles of simulated reflectivity curves for different densities were determined for both materials, with relative densities ranging from ρ*rel* = 90-100%. Figure 6 shows the  values of the calculated  plotted versus the simulated densities; calibration curves were obtained using linear curve fits (dashed lines; R2 > 0.995). The average measurement error was estimated to be within 1.0%. As expected, a 100% theoretical density for both single crystal substrates was found within the error margin of the measurement: Al2O3 100.7 ± 1.0% and ZnO 99.9 ± 1.0%. The accuracy is thus comparable or even higher than methods such as RBS and ellipsometry, without the need for complex models or calculations.

**4.3 X-ray Reflectivity of Thin Films on a Substrate**

Prior to simulating the reflectivity curves and preparing the calibration curves, test samples were made. The influence of the annealing temperatures on the surface roughness (by AFM) and the average film thickness (by SEM) were determined. For samples annealed at 650, 850, and 1000 ºC, the average RMS surface roughness was approximately 0.3, 0.5, and 0.9 nm, respectively. Since the layer thickness of the film is determined presumably by only a few particles, the observed exponential increase in surface roughness is closely related to the particle growth at increasing temperatures [24]. The average film thickness of samples annealed between 650 and 1000 ºC was determined, and ranged from approximately 75 to 65 nm, respectively. All calibration curves were simulated using an average film thickness of 70 nm. The changing surface roughness with increasing annealing temperature was taken into account, however.

Cross-sectional SEM was used to verify the homogeneous distribution of particles in the deposited films. A homogeneous layer is important, because with XRR the density information is extrapolated from the derived density of the top-layer. For sol-gel-derived films, the densification is rather difficult to control due to strain caused by the substrate, by crystal growth, or by homogeneous and heterogeneous crystallization in the bulk and at the interface, respectively [8,25]. All these phenomena can cause different densification behavior in the thin film or at the thin film-substrate interface (density gradient), which may lead to deviations in the XRR curves, and thus in the calculated densities. For such films, more parameters are needed in the simulations, and a density gradient should be taken into account (available in the software) [17].

Figure 7 schematically shows how the XRR method was used for a thin film annealed at 850 ºC. First, an XRR curve was recorded, and the  was determined by the first minimum of the 3rd derivative (Figure 7d). The density was then determined by the corresponding position of the  in the calibration curve (Figure 8).

All heat treated samples were measured at least five times. For the annealing temperatures 650, 850, and 1000 ºC, the density was determined to be 83.7%, 89.6%, and 91.6%, respectively (Figure 9). The observed trend (dashed line) in densification coincides well with what is generally expected for sintering.

*4.3.1 Validation Results with RBS & SEM analysis*

To check the validity of our method, the density of the abovementioned samples was verified by a combination of RBS and SEM cross-sectional analysis. RBS analysis yielded the total concentration of (Zr+Y) atoms/cm2, from which the mass/cm2 could be calculated. The mass per volume ratio was calculated from the sum of the individual atoms, according to:

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| --- | --- | --- |
|  |  | Eq. (16) |

where  is the total mass per area, *Xi* and *MWi* are the total number of atoms and the molecular weight of species type *i*, respectively, and NA is Avogadro’s number. In combination with the film thickness derived from cross-sectional SEM analysis, the density of the samples was determined with a combined error of both techniques of approximately 5.0%, due to elemental inaccuracy, and statistical and systematic errors.

The results are summarized in Table 3. As shown, the total YSZ mass deposited on the three samples is almost equal, indicating that the sol-gel deposition method is very reproducible, and batch-to-batch errors can be neglected. The differences in the density are thus only determined by shrinkage of the sol-gel film during heat treatment. Figure 9 summarizes the results obtained using the XRR method and a combination of RBS and SEM. The density values determined using the XRR method are well within the error margin of the established analytical techniques. Also, the densification behavior of the thin film follows the same trend. These results clearly demonstrate that our method is a fast, simple and accurate method to determine the density of sol-gel derived materials.

**5. Conclusions**

We have successfully demonstrated a simple and fast approach to determine the density of sol-gel derived ceramic thin films using XRR. The method shows no apparent effect of changing sample size, interface roughness, or film thickness of different samples on the final determined density, and has an average measurement error of only 1%. A *pseudo*-critical angle was determined from the first minimum of the 3rd derivative of the reflectivity curves. Simulations of films of various densities were used to obtain calibration curves, where the calculated  was plotted versus the material density. Subsequently, the experimental thin film density was determined using these calibration curves according to the position of the determined *pseudo*-critical angle. The method was validated by determining the density of single crystal Al2O3 and ZnO substrates (ρ*rel* = 100%) within 1% of the expected value. The density of ceramic thin YSZ films heat treated at 650, 850, and 1000 ºC were calculated using XRR, and validated using a combination of well-established techniques such as RBS and SEM analysis. The density values obtained using the XRR method were well within the error margin of the combined RBS and SEM analysis, and the same trend in densification was observed. The XRR method can be used to study the impact of sintering temperature and substrate strain on densification behavior of sol-gel derived ceramics. Also the densification of amorphous gels, as a result of dehydroxylation and surface contraction during drying can be studied, since XRR does not rely on diffraction. Thus, new possibilities emerge to follow the sol-gel process in depth from the liquid phase (precursor solution), *via* gel formation to the final crystalline ceramic film.

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**References**

1. Wang X, Atkinson A (2011) Microstructure Evolution in Thin Zirconia Films: Experimental Observation and Modelling. Acta Mater 59 (6):2514-2525

2. Hendriks MGHM, Heijman MJGW, van Zyl WE, ten Elshof JE, Verweij H (2001) Solid State Supercapacitor Materials: Layered Structures of Yttria-stabilized Zirconia Sandwiched between Platinum/Yttria-stabilized Zirconia Composites. J Appl Phys 90 (10):5303-5307

3. Butz B, Störmer H, Gerthsen D, Bockmeyer M, Krüger R, Ivers-Tiffée E, Luysberg M (2008) Microstructure of Nanocrystalline Yttria-doped Zirconia Thin Films obtained by Sol-gel Processing. J Am Ceram Soc 91 (7):2281-2289

4. Gaudon M, Djurado E, Menzler NH (2004) Morphology and Sintering Behaviour of Yttria Stabilised Zirconia (8-YSZ) Powders Synthesised by Spray Pyrolysis. Ceram Int 30 (8):2295-2303

5. Swanepoel R (1983) Determination of the Thickness and Optical Constants of Amorphous Silicon. Journal of Physics E: Scientific Instruments 16 (12):1214-1222

6. Díaz-Parralejo A, Caruso R, Ortiz AL, Guiberteau F (2004) Densification and Porosity Evaluation of ZrO2-3 mol.% Y 2O3 Sol-gel Thin Films. Thin Solid Films 458 (1-2):92-97

7. Jerman M, Qiao Z, Mergel D (2005) Refractive Index of Thin Films of SiO2, ZrO2, and HfO2 as a Function of the Films' Mass Density. Appl Opt 44 (15):3006-3012

8. Scherer GW (1997) Sintering of Sol-Gel Films. J Sol-Gel Sci Technol 8 (1-3):353-363

9. Brinker CJ, Scherer GW (1990) Sol-gel Science: the Physics and Chemistry of Sol-gel Processing. Academic Press, Inc, San Diego, CA

10. Jellison Jr GE (1998) Spectroscopic Ellipsometry Data Analysis: Measured Versus Calculated Quantities. Thin Solid Films 313-314:33-39

11. Birkholz M, Fewster PF, Genzel C (2006) Thin Film Analysis by X-ray Scattering. Wiley-VCH Verlag GmbH, Weinheim

12. Als-Nielsen J, McMorrow D (2011) Elements of Modern X-ray Physics. John Wiley & Sons, Chichester, West Sussex

13. Daillant J, Gibaud A (2009) X-ray and Neutron Reflectivity: Principles and Applications. Springer-Verlag, Berlin Heidelberg

14. Vives S, Meunier C (2010) Densification of Amorphous Sol-gel TiO2 Films: An X-ray Reflectometry Study. Thin Solid Films 518 (14):3748-3753

15. Lenormand P, Lecomte A, Babonneau D, Dauger A (2006) X-ray Reflectivity, Diffraction and Grazing Incidence Small Angle X-ray Scattering as Complementary Methods in the Microstructural Study of Sol-gel Zirconia Thin Films. Thin Solid Films 495 (1-2):224-231

16. Morelhão SL, Brito GES, Abramof E (2002) Nanostructure of Sol-gel Films by X-ray Specular Reflectivity. Appl Phys Lett 80 (3):407-409

17. Bruker (2009) DIFFRACplus LEPTOS 7 User Manual. Bruker AXS GmbH, Karlsruhe, Germany

18. Compton AH (1923) A Quantum Theory of the Scattering of X-rays by Light Elements. Physical Review 21 (5):483-502

19. Prince E (2006) International Tables of Crystallography, Volume C: Mathematical, Physical and Chemical Tables. Springer Netherlands,

20. Parratt LG (1954) Surface Studies of Solids by Total Reflection of X-rays. Physical Review 95 (2):359-369

21. Kiessig H (1931) Interferenz von Röntgenstrahlen an Dünnen Schichten. Annalen der Physik 402 (7):769-788

22. Nevot L, Croce P (1980) Characterization of Surfaces by Grazing X-Ray Reflection - Application to Study of Polishing of some Silicate-Glasses. Revue De Physique Appliquee 15 (3):761-779

23. Veldhuis SA, George A, Nijland M, ten Elshof JE (2012) Concentration Dependence on the Shape and Size of Sol–Gel-Derived Yttria-Stabilized Zirconia Ceramic Features by Soft Lithographic Patterning. Langmuir 28 (42):15111-15117

24. Kang SJL (2005) Sintering: Densification, Grain Growth, and Microstructure. Butterworth-Heinemann, Oxford

25. Schwartz RW (1997) Chemical Solution Deposition of Perovskite Thin Films. Chem Mater 9 (11):2325-2340

**Tables**

Table 1 Overview of available methods for the density determination and their properties.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Technique** | **Based on** | **Error** | **Advantages** | **Disadvantages** |
| Archimedes | Volume displacement | n.d. | Simple, fast | Not applicable for thin films |
|  |  |  |  |  |
| SEM | Contrast particles/pores | n.d. | Widely applicable | Assumes fraction 2D cross-section is equivalent in 3D, laborious processing |
|  |  |  |  |  |
|  | Difference in film thickness dense/porous | n.d. | Simple | Knowledge of densification behavior necessary |
|  |  |  |  |  |
| Swanepoel | Refractive index | < 1% | Non-destructive, simple, fast, film thickness | Only valid for transparent substrates, applicable for films < 300 nm |
|  |  |  |  |  |
| RBS | Recoil He2+ ions off sample surface | 1-5% | Non-destructive, whole periodic table (Z > 6) covered, stoichiometry, depth-profiling, film thickness | Not sensitive to all elements, expensive, slow |
|  |  |  |  |  |
| Ellipsometry | Reflectance of a polarized light beam | < 1% | Non-destructive, fast, high resolution, film thickness | Indirect, difficult data interpretation (*via* modeling) |
|  |  |  |  |  |
| XRR | Total external reflection under low incidence angles | < 1% | Non-destructive, fast, small number of fitting parameters, film thickness/roughness | Difficult to determine the density of imperfect films |

n.d. = not determined / unknown

Table 2 Parameters for the X-ray reflectivity simulations.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Thickness  [nm] | RMS roughness  [nm] | Density  [g/cm3] |
| 3YSZ | 50 - 300 | 0 - 2.000 | 5.05 - 6.05 |
| Al2O3 substrate | ∞ | 0.150 | 3.984 |

Table 3 Thin film densities of spin-coated 3YSZ films on sapphire substrates calculated by a combination of RBS and SEM analysis.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| RBS | | | | | | SEM | Density | |
| Temperature | Element [at/cm2] | | | Total | | Thickness | Abs. | Rel. |
| [ºC] | Zr | Y | O | [at/cm2] | [µg/cm2] | [nm] | [g/cm3] | [%] |
| 650 | 1.7·1017 | 1.1·1016 | 3.6·1017 | 5.3·1017 | 3.66·10-5 | 73.1 | 5.022 | 83.0 ± 5% |
| 850 | 1.7·1017 | 1.1·1016 | 3.6·1017 | 5.4·1017 | 3.68·10-5 | 67.4 | 5.461 | 90.3 ± 5% |
| 1000 | 1.7·1017 | 1.1·1016 | 3.6·1017 | 5.4·1017 | 3.68·10-5 | 65.7 | 5.603 | 92.6 ± 5% |

**Figures**

**Fig. 1**

Schematic representation of the reflection and transmission of a film of infinite (substrate) and finite (thin film) thickness. (a) an X-ray beam impinges the surface of a polished substrate on very low angle, ,  and  are the angle of incidence, reflection, and refraction (transmittance), respectively. The vertical wave vectors of the incident and transmitted beam are described by  and , respectively; (b) as the X-ray beam impinges a finite thin film (thickness Δd), a phase shift related to the difference in refractive index between film and substrate is observed, and an infinite sequence of reflections is possible.

Fig. 2

Simulated reflectivity curves according to Parratt’s formalism, see Eq. (11) and Eq. (12), with a fixed critical angle of = 0.65º. At increasing layer imperfection, the absorption of X-rays into the films increases, and thus the coefficient  increases. The determination of the critical angle of total external reflection then becomes increasingly difficult.

Fig. 3

Influence of different fitting parameters on the X-ray reflectivity simulations, where ρ, d, and Rq are the film density, thickness, and interfacial roughness, respectively. The simulated curves are based on a 3 mol% yttria-stabilized zirconia (3YSZ) film deposited on a sapphire single crystal substrate: (a) at increased density, the reflectivity curve (and critical angle) shifts linearly to higher angles; (b) at increased film thickness, the periodicity of the Kiessig fringes decreases according to ; (c) at increased interface roughness, a more rapid intensity drop is observed at angles .

**Fig. 4**

Schematic representation of the sample alignment. The x- and y-axis are aligned at the center of the sample. Subsequently, the height of the sample is aligned at the center of the direct X-ray beam by changing the z-axis. Finally, possible sample tilt perpendicular and parallel to the beam path is corrected with a - and -scan, respectively.

Fig. 5

Numerical calculation of the *pseudo*-critical angle used for the density determination of thin films: (a) simulated X-ray reflectivity curve of a 50 nm thin 3YSZ film (ρ = 6.05 g/cm3; Rq = 0.500 nm) on a Al2O3 single crystal substrate (Rq = 0.150 nm). The dashed black lines show the steep intensity increase at angles  observed for samples of decreasing size (*i.e.* beam footprint). (b) 1st derivative; (c) 2nd derivative; and (d) 3rd derivative of the calculated XRR curve. The first minimum of the 3rd derivative determines the *pseudo*-critical angle. No differences are observed in the calculation of this point as a result of decreasing sample size.

Fig. 6

Reflectivity curves for both Al2O3 and ZnO single crystals were simulated at different densities, and plotted versus the calculated *pseudo*-critical angle. The calibration curve was obtained by using a linear curve fit (dashed line). The single crystal substrates were measured five times; the average value and error bars were plotted (red square/dot and bars, respectively).

**Fig. 7**

Determination of the *pseudo*-critical angle for a 3YSZ thin film on a single crystal Al2O3 substrate annealed for 1 h at 850 ºC in air, by using the first minimum of the numerically calculated 3rd derivative. (a) the measured reflectivity curve, and its (b) 1st derivative; (c) 2nd derivative; and (d) 3rd derivative. When the measured reflectivity curve is plotted with a logarithmic intensity scale, the Kiessig fringes at higher angles are more pronounced, see inset in (a).

**Fig. 8**

The relative density of a 3YSZ thin film on a single crystal Al2O3 substrate annealed for 1 h at 850 ºC in air (ρrel = 89.6%) is calculated in the calibration curve by using the  determined in Figure 7. The data points of the calibration curve are based on simulations of thin 3YSZ film with a film thickness of 70 nm, a RMS surface roughness of 0.500 nm, and densities ranging from ρ = 5.05-6.05 g/cm3.

**Fig. 9**

Comparison between derived thin film density of the proposed XRR method and the combined RBS and SEM analysis, as a function of the annealing temperature. The results obtained *via* the XRR method are well within error margin of the established techniques. The dashed lines are exponential fits to guide the eye.