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Comprehensive environmental testing of optical properties in thin films

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Abstract

Environmental characterization of optical and structural properties of thin films continues to be a challenging task. To understand the failure mechanism in high temperature thin film applications, it is crucial to understand how material properties change with temperature. An accurate knowledge of the variation of the dielectric function of thin films and its relation to compositional and microstructural changes could help to prevent failures. This article presents an environmental in-situ characterization methodology that combines the study of the optical constants in an environmental chamber by spectroscopic ellipsometry, with compositional depth profile analysis using ion beam analysis techniques and a structure analysis by Raman spectroscopy. The main novelty of this methodology is that all analytical techniques are carried out sequentially in a multi-chamber cluster tool without sample exposure to undefined atmospheres. Carbon-titanium metal thin film had been studied following the described characterization methodology.

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1. Introduction

Nowadays, thin films and coatings are being applied in a wide range of technologies. Increasingly, coatings need to be designed for applications where they have to withstand more extreme environmental conditions. This requires not only the development of new thin films materials but also a better understanding of those coatings. High temperature applications such as coatings for thermal barriers on superalloys in engines, thin films for high temperature gas sensors or strain-gauges or coatings for solar thermal applications among others [1–4], require an in-depth study of thin films properties at high temperatures. In some of these applications, the coatings are applied in a vacuum, but frequently they are exposed to extreme environments.

Depending on the deposition mechanism employed and also on the environment and the working temperature a coating is designed for, its failure mechanism can be different.

Some of the most common failure mechanisms related with high temperature or extreme conditions are thermal expansion, temperature-induced oxide growth [1], changes in the microstructure, diffusion or segregation of some internal layers to the surface, electrochemical corrosion, hybridization of oxide, evaporation of volatile components or combination of one or more modes [5]. Thermal stresses frequently arise due to temperature changes if the different layers do not have the same coefficient of thermal expansion (CTE). When the stress is high, it can produce deformation, fracture and delamination or de-cohesion of the films. A comprehensive analysis of the failure mechanism in thin films should combine the study of how composition, microstructure and optical constants vary, associated with changes in the environment and in temperature. Furthermore, the properties of materials in the form of thin films can be different from those of the same materials in bulk form. In order to predict and improve the reliability of thin films under extreme

environmental conditions, it is necessary to characterize optical and structural properties versus temperature in the same experimental setup.

Optical and structural characterization has frequently been performed independently. Real time spectroscopic ellipsometry (SE) has proved to be a powerful tool for investigating optical constants in metals, semiconductors and dielectric materials. It can be used during in-situ growth of samples installed inside a deposition chamber [6], or at different temperatures to observe changes of the coating with temperature [7]. It has also been used inside a vacuum chamber in order to study the temperature dependence of the dielectric function and the optical transitions for thin films with thermally tunable optical constants [8,9]. Raman spectroscopy and ion beam analysis techniques have been widely applied to characterize chemical bonding and atomic composition respectively [10], but commonly both techniques are used in different set ups suffering from possible oxygen incorporation when the samples are moved from one characterization device to the other.

In order not to break the vacuum during characterization, and to give the possibility of characterizing many properties of materials in a connected multi-chamber device, various approaches have been designed. A *cluster tool* is namely a tool that allows making multi-steps experiments. Some *cluster tools* with ultra-high vacuum technologies and different characterization chambers have been employed. For instance, the *cluster tool* at Forschungszentrum Jülich GmbH (Germany) is dedicated to the study of magnetism and spintronics within an ultrahigh vacuum (UHV) environment [11]. In Princeton University, there is a four chamber UHV *cluster tool* that allows in situ structural analysis [12], and there is another *cluster tool* situated at the faculty of physics at the RWTH Aachen (Germany) [13]. In all these, the

samples cannot be exposed to different temperatures and atmospheres, thus making them unsuitable for *in-situ* environmental characterization.

In this work, we present a novel methodology for environmental high temperature tests that integrates complementary characterization techniques into a single device. The new *cluster tool* situated at Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Germany, includes thin films characterization techniques such as spectroscopic ellipsometry, Raman spectroscopy, and ion beam analysis in several environmental conditions and at different temperatures.

The methodology outlined in this article has been tested for a carbon-titanium nanocomposite thin film deposited by pulsed filtered cathodic vacuum arc. Those samples have been exposed to an in-situ heating process while measuring spectroscopic ellipsometry. Before and after heating, the thin films were characterized with Raman spectroscopy and Rutherford Backscattering Spectroscopy (RBS) in order to analyze the compositional and microstructural changes occurred during the heating process.

2. Experimental methods

The in situ high vacuum modification and analysis system consists of three characterization chambers. A general view of the cluster tool is shown in Fig. 1. The environmental chamber (E-C), the analysis chamber (A-C), and the ion beam analysis chamber (IBA-C) are shown. A central distribution chamber connects all the different units and enables in-situ access to the different tools without leaving vacuum. All experimental chambers offer the possibility of heating the samples through a heatable sample holder which can reach up to 1000°C.

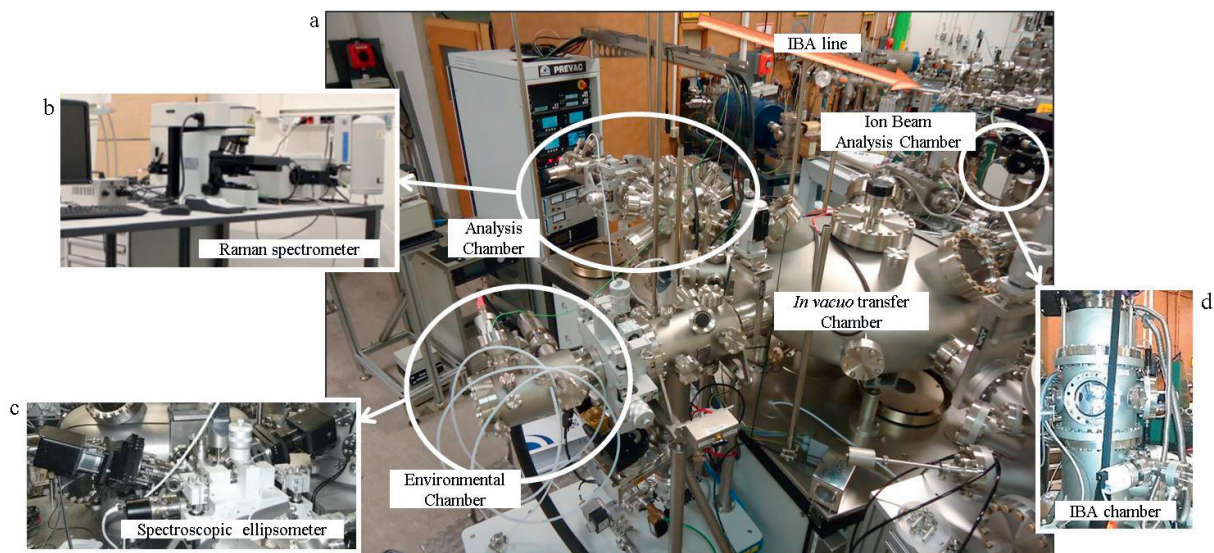


Fig. 1.: (a) Top view of the cluster tool: the central distribution chamber connects the different units and allows in-situ access to all preparation and characterization tools without breaking the vacuum (b) the analysis chamber contains the in-situ Raman spectrometer; (c) the environmental chamber houses the real time spectroscopic ellipsometry with different possible simulated environments; (d) the ion beam analysis chamber connected to the 6 MeV accelerator allows characterization of the samples by different IBA techniques (RBS, NRA, ERD).

2.1. In-situ spectroscopic ellipsometry

The E-C houses a real time spectroscopic ellipsometer (SE) and includes the possibility of simulating different environmental conditions. In-situ SE can be carried out in vacuum conditions as well as in controlled atmospheres containing O₂, N₂ and Ar, or water vapor. A turbo pump equipped with a butterfly valve helps to limit the gas inlet in environmental operation.

The optical properties of the thin films in the energy range of 1.24 to 3.34 eV at an angle of incidence of 70° can be determined by spectroscopic ellipsometry (SE) using a rotating compensator ellipsometer M-2000FI (J. A. Woolam, Inc.) installed inside the environmental chamber. The acquired data is analysed using WVASE software (J. A. Woolam, Inc.).

Ellipsometry can determine optical constants and thicknesses of thin films by fitting a parameterized model to the measured data, as a function of environmental conditions. The fitting procedure is described more fully elsewhere [14]. The ellipsometric parameters amplitude (ψ) and phase difference (Δ) are related to the complex reflection ratio (ρ) for parallel polarized light (R_p) and perpendicular polarized light (R_s), relative to the plane of incidence, by the following formula:

$$\rho = \frac{R_p}{R_s} = \tan(\psi)e^{i\Delta} \quad (1)$$

To determine the variation in the ellipsometry parameters at different temperatures or environments, the integrated area between 1.5 to 2.5 eV of both parameters are added at each temperature (SE_T), as described in equation (2). This energy region is selected because it is the region where the ellipsometric parameters (ψ , Δ) have higher accuracy which allows for a more precise tracking.

$$SE_T = \int_{1.5eV}^{2.5eV} \psi_T dE + \int_{1.5eV}^{2.5eV} \Delta_T dE \quad (2)$$

The variation of the ellipsometry parameters between two temperatures is described by the following equation:

$$\Delta(SE) = 100 \times \left| \frac{SE_{T2} - SE_{T1}}{SE_{T1}} \right| \quad (3)$$

2.2. Ion beam analysis techniques

The IBA-C of the *cluster tool* is connected to the 6 MV Tandem ion accelerator, which can provide ions of different nature and charge state. In this chamber, ⁴He²⁺ ions with up to 4 MeV energy, ²D⁺ up to 1.8 MeV and ³⁵Cl⁷⁺ up to 14MeV energy can be employed to carry out several ion beam analysis and characterization techniques.

The ions impinge the sample and can be elastically backscattered thus giving rise to Rutherford backscattering spectroscopy (RBS). This provides depth-resolved

compositional information for heavier elements in thin films up to ~1 μ m thickness.

Furthermore, the incident ions can expel atoms from the sample. The debris can be detected which enables elastic recoil detection (ERD) analysis. This technique provides depth-resolved compositional information for the lighter elements up to a depth of ~0.5 μ m.

Finally, the energetic ions may be captured by the sample's nuclei which then transition to metastable intermediate states. Their eventual decay leaves detectable products and allows for nuclear reaction analysis (NRA). It is highly specific as typically the species of the incident ion and its energy have to be chosen very carefully in order to trigger the reaction of interest. NRA is particularly useful when the low energy part of the NRA spectrum is analyzed for elastically backscattered ions. This allows for the simultaneous identification of the heavier elements by RBS and in addition one lighter element by means of NRA..

Together the mentioned techniques allow identification of the overall composition and the compositional depth profile of thin films. The technique, or the combination of techniques, used in each case will depend on the characteristics of the sample [15].

Moreover, the sample holder in the IBA-C is heatable up to 1000°C, allowing a non-destructive compositional analysis of the samples at different temperatures, as well as depth profile composition monitoring.

2.3. Structure analysis

The A-C is equipped with a Raman spectrometer. Chemical bonding and solid state structure of many thin films materials can be studied by a careful analysis of their Raman spectra.

A modular fibre-coupled iHR 550 Raman spectrometer equipped with 3 changeable gratings (1800/mm, 600/mm, 300/mm) is connected to the A-C. Two lasers, a green one with a wavelength of 532 nm, and a blue one with 473 nm are available. In situ operation is possible by two fibre-coupled remote Raman heads (one for each wavelength). The incorporation of a TV camera would allow for a close visualization. The back illuminated deep depletion CCD detector with 90% quantum efficiency in the spectral range from 400 nm to 800 nm helps to keep the measurement times at bay.

As in the IBA-C, the sample holder in the A-C is heatable, allowing the study of the variation of the chemical bonding of the samples at different temperatures in a non-destructive manner.

2.4. Visual inspection

Visual inspection can be also very useful to examine sample deterioration. Depending on the sample and the type of failure, it is possible to detect surface cracks, delamination of the coating, extreme change or color, the migration of elements from the substrate to the surface. Therefore, after each heating step, it could be necessary to verify the integrity of the sample before the next heating step. The camera of the

A-C allows visual sample evaluation in order to decide whether the characterization procedure needs to be stopped because there was a catastrophic failure of the film.

3. Environmental characterization methodology

The following steps should be followed to run a complete thermal characterization process as shown in Fig. 2.

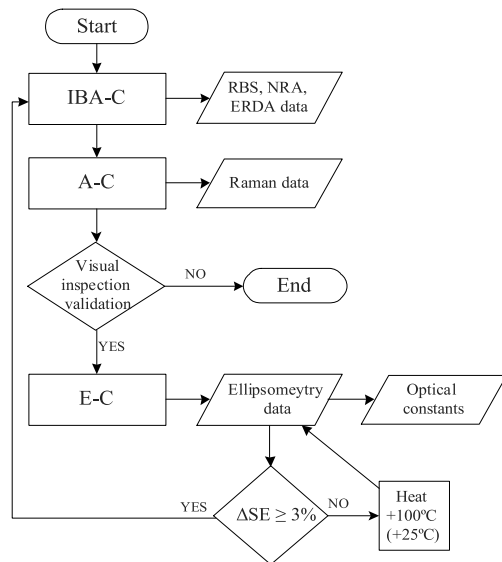


Fig. 2. Flow chart of the methodology described for high temperature testing of thin films. The different chambers represented in the diagram: the analysis chamber (A-C), the environmental chamber (E-C) and the ion beam analysis chamber (IBA-C).

1. Installation of the sample in the transfer chamber.
2. Transfer of the sample to the IBA-C to examine its elementary composition and its depth distribution along the thickness. All elements of the periodic table can be detected by IBA, so the methodology chosen between all the available in the IBA-C depends on the type of sample.
3. Sample transfer to the A-C. Measure with Raman spectroscopy if desired.
4. Visual inspection of the state of the sample in the A-C. In the case of sample deterioration, the characterization process is finished. If no visual failure is observed, continue with the next step.
5. Transfer the sample to the environmental E-C. Measure using in-situ spectroscopic ellipsometry (SE). Depending on the type of sample and desired study, it is possible to do SE in vacuum or in a controlled environment as described above.
6. Increase the temperature by 100°C (only until the first changes are measured. upon beginning deterioration round, increase by 25°C) and measure the ellipsometry parameters (Δ , φ) at each temperature in the whole energy range.

7. If SE value (defined in eq. (2)) does not change by more than 3% as described in eq. (3) go to the previous step increasing the temperature by 100°C (25°C after the first changes).
8. If $\Delta(SE) \geq 3\%$, stop heating, and perform final IBA and Raman characterization.

4. Measurement example: amorphous carbon-titanium thin film for high-temperature applications

Carbon-transition metal films have been studied for their many possible applications due to their high melting points and spectral selectivity [16,17]. In this paper, the characterization of a carbon-titanium thin film is shown as an example of the in-situ characterization methodology described above.

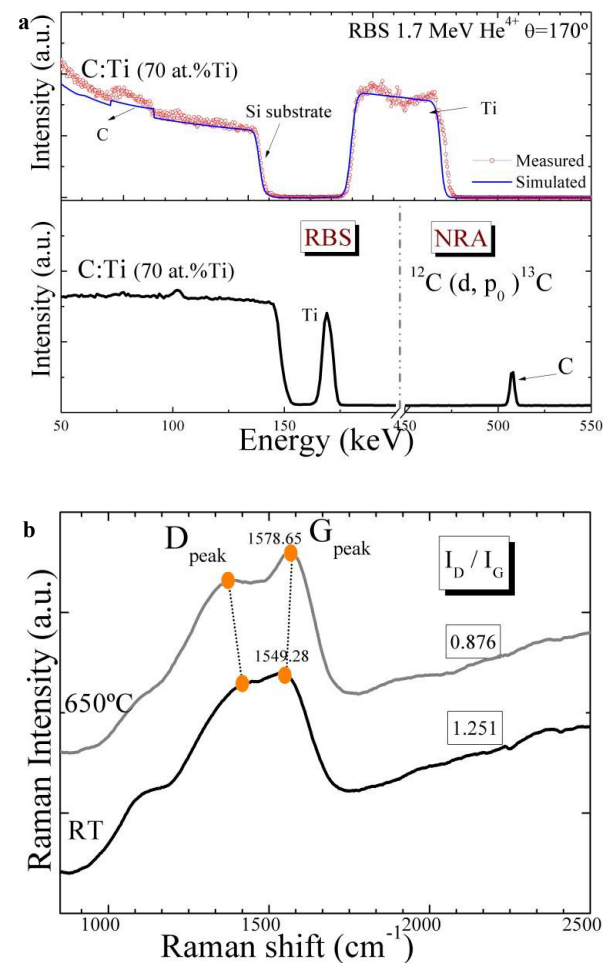


Fig. 3. (a) RBS and NRA ion beam analysis of carbon - titanium (70 at.% Ti) sample deposited with PFCVA technique on Si (100); (b) Normalized Raman spectra at different temperatures with 532 nm excitation light of the same sample but deposited on stainless steel substrate.

The C:Ti sample was grown on Silicon (100) and Stainless Steel (316L) substrates by means of a pulsed filtered cathodic vacuum arc system (PFCVA-450, Plasma Technology

Limited, Hong Kong). The sample were grown by the co-evaporation of carbon and titanium, using two cathodic arc sources, one equipped with a carbon cathode and the other one with a titanium cathode. More details about similar thin film deposition can be found in literature [18].

Following the characterization methodology described in section 3, firstly the samples are introduced in the IBA-C. To determine the amount of carbon and metal accurately combined Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA) were used. The RBS spectra were collected with ^4He ions with an energy beam of 1.7 MeV, using a silicon barrier detector located at a backscattering angle of 170° , and an energy resolution of 13 keV. The thickness of the sample has been previously measured with confocal microscopy, so the elementary areal density and the depth profile can be obtained directly with this measurement, fitting the spectra with the software SIMNRA [19]. For the NRA measurements, deuterium ions were employed as incident particles with 1.248 MeV and a detection angle of 135° to induce the nuclear reaction $^{12}\text{C}(d,p)^{13}\text{C}$ [20,21]. The areal densities were estimated by comparing the measured intensities to those of samples of known composition. As shown in Fig. 3 (a) 70 at.% of Ti is found. It can be observed that titanium is uniformly distributed along the thickness of the deposited sample.

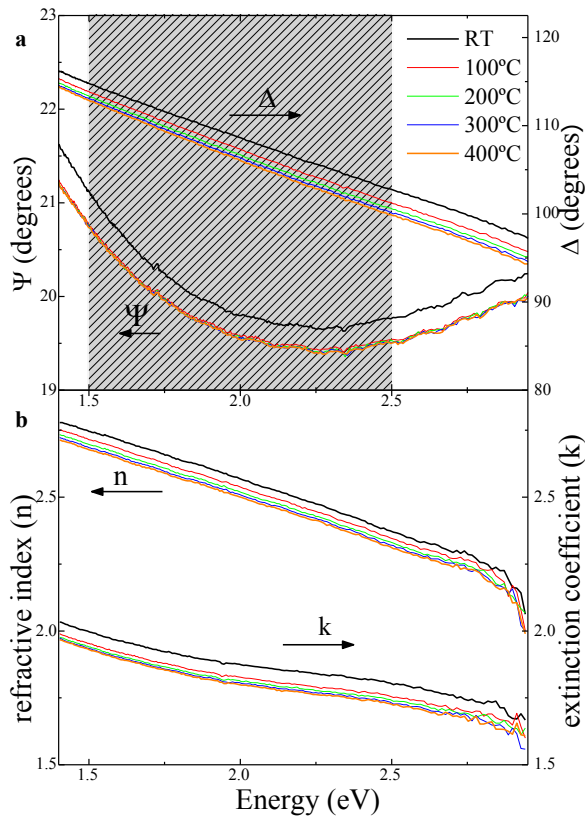


Fig. 4. (a) Ellipsometry data at different temperatures of carbon - titanium (70 at.% Ti) sample deposited with PFCVA technique on Si (100); (b) Complex refractive index (n , k) obtained from the ellipsometry data.

Fig. 3 (b) shows the Raman spectra of the C:Ti thin films as deposited and after heating 650°C , in the wavenumber range of 800 to 2500 cm^{-1} measured with 532 nm excitation light. The D and G peaks and the Si peak at $\sim 520\text{ cm}^{-1}$ (not shown) can be observed for both temperatures. To obtain quantitative understanding of the temperature dependence structural changes of the films, the Raman spectra were fitted by a combination of an exponential background, a symmetric Lorentzian for the D peak and an asymmetric Breit-Wigner-Fano (BWF) shape for the G peak [22]. The intensity of the D peak is significantly lower than that of the G peak region, and this difference increases with temperature. After annealing at 650°C , the G peak is clearly defined and it shifts towards higher wavenumbers from ~ 1550 to 1580 cm^{-1} , while D peak position decreases slightly. The I_D/I_G ratio dispersion decreases with temperature (from ~ 1.21 at RT to ~ 0.876 at 650°C). The presence of the D band indicates the presence of aromatic rings in the sp^2 phase of the carbon, while the I_D/I_G ratio is related with the size of these aromatics clusters in disordered carbons. As reported before [23], in the C:Ti deposited thin films, we have 6-fold ring clusters and the average cluster size higher than in pure carbon films. The decrease in the G peak at increasing temperature indicated the graphitization of carbon, and the promotion of the nucleation and growth of 6-fold ring clusters by the presence of the Ti. This indicates that the Ti nanoparticles act as nucleation centers of 6-fold rings at low temperatures while at high temperatures the Ti favors the ordering within the clusters [24].

Once the elementary distribution and the chemical bonding are analyzed, the sample is transferred to the E-C. The optical constants of the C:Ti thin film were determined by spectroscopic ellipsometry (SE) using the in-situ ellipsometer situated inside the E-C.

In this example, the sample was measured during a heating ramp from room temperature to 650°C in vacuum, in the energy range of 1.24 to 3.34 eV at an angle of polarized light incidence of 70° . The ellipsometry data Δ and Ψ measured are shown in Fig. 4 (a). The data were acquired and interpreted via modeling using WVASE32 software. To obtain the complex index of refraction (n) and the extinction coefficient (k) from ellipsometry data a model has to be applied to calculate of the optical response and make a regression analysis. For absorbing materials with quasi infinite film thickness, like C:Ti studied here, the thickness of the layer is not a parameter to consider in the calculation. With this method, the optical constants n , and k can be immediately estimated from Δ and Ψ using the semi-infinite medium approximation and point-by-point fitting as they were bulk materials. They are shown in Fig. 4 (b) at different temperatures. Both n and k decrease with temperature when we start heating at the first step between RT and 100°C , but they stay more stable at higher temperatures.

5. Summary and Outlook

A novel in-situ thermal measurement characterization methodology for thin films has been presented to investigate

the compositional, optical and structural changes in a wide range of temperatures and environments.

The main advantage of the proposed methodology is the possibility of doing different measurements sequentially in the same multi-chamber *cluster tool*, without breaking the vacuum, avoiding the oxygen enrichment of the samples. Other advantages are the possibility of combining optical and structural characterization analysis and the presence of a heatable sample holder in all the chambers, allowing characterization of the samples at different temperatures and environments. With all this capabilities, it is possible to have a better understanding of the failure mechanisms at high temperatures in a wide variety of thin films or coatings.

As an example of the versatility and the great potential of the system, the methodology was applied to a carbon-titanium thin film deposited by pulsed filtered cathodic vacuum arc. Changes in both chemical bonding and optical constants with increasing temperature were recorded in a single experiment.

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