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Sputter-deposition of ultra-thin film stacks from EUROFER97 and tungsten: characterisation and interaction with low-energy D and He ions

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Abstract

We have sputter-deposited stacks of ultrathin layers from EUROFER97 and tungsten on silicon substrates. Ion beam analysis techniques are used for composition characterisation and microscopy methods are employed for structural examination. The films are subsequently studied by time-of-flight low-energy ion scattering (ToF-LEIS) for primary 10 keV He⁺ and 8 keV D⁺ ions to demonstrate an approach of providing accurate and precise experimental reference electronic stopping cross-sections for fusion-relevant steels. The energy-converted ToF-LEIS spectra are compared to Monte-Carlo simulations for quantitative analysis explicitly considering the influence of plural and multiple scattering. We discuss the deduced stopping cross-sections of EUROFER97 in comparison to predictions by SRIM using Bragg’s rule of stopping power additivity.

1. Introduction

As a reduced activation ferritic-martensitic (RAFM) steel, EUROFER97 is a candidate structural material to be used in the first wall and breeding blanket of the demonstration nuclear fusion reactor (DEMO) [1]. It is comprised of a nominal atomic composition of 9.5% Cr and 0.33% W as well as several residual elements including C, Mn, V and Ta, balanced by Fe [2].

While EUROFER97 or similar reduced activation steels are not expected to be directly exposed to the harsh conditions of the fusion plasma which can rapidly degrade plasma-facing components (PFCs) [3], as an integral component of the wall, it is expected to be joined with PFCs and thus, be subject to increased temperatures, radiation as well as wall-diffused fuel species. Studying the interfacing of this material and PFC-candidate materials is thus a topic of continual interest [4, 5]. In this context, low-energy ions have been extensively used to study near-surface properties of EUROFER97 which are relevant for such component interfacing as well as potential unexpected plasma exposure [6–8].

The mean energy deposition per unit path length \( \frac{dE}{dx} \) by an ion to the electronic system of the target is defined as the stopping power of the material for the respective ion. The stopping cross-section (SCS, \( \varepsilon \)) is defined as \( \varepsilon = 1/N\frac{dE}{dx} \) where \( dE \) is the mean energy lost by the energetic ion passing dx length in a target material of atomic volume density N [9] yielding a quantity independent of gravimetric density. Both \( \frac{dE}{dx} \) and \( \varepsilon \) are key quantities to describe ion-matter interaction as they allow to establishment of depth scales in the analytical approach and ion range in irradiations. Quantitative knowledge of the electronic SCS of low-activation steels for plasma species is thus not only an essential input parameter for simulating potential plasma exposure and radiation damage as well as in hindsight of potential steel-based devices, but also a prerequisite for quantitative depth profiles in post-mortem analysis using low-energy ion beams in e.g. (time-of-flight) low-energy ion scattering (ToF-LEIS, secondary ion mass spectrometry (SIMS) or related techniques [8, 10, 11]. At present, however, no experimental reference electronic stopping power at energies below the Bragg peak [12] for
any steel including EUROFER97 exists [13]. Only extrapolations using Bragg’s rule of stopping power additivity [14] in semiempirical models such as SRIM [15] are available. Readily available predictions by static Density Functional Theory (DFT) have been demonstrated to lack accuracy for a range of early transition metals even in the case of low-energy protons [16]. Time-dependent DFT as an emerging tool is predicting the complex behaviour of compound materials [17] with recent approaches also addressing more complex charge transfer phenomena for helium [18]. To further benchmark these novel theoretical approaches and to improve SRIM predictions for any kind of steel, experimentally deduced reference stopping cross-sections are thus highly desirable.

The electronic stopping power of materials for light ions can be measured in different approaches, with backscattering from thin films being an established approach [9]. Initially used for energies around and above the Bragg peak, this approach has been successfully employed to measure stopping cross sections from ultrathin films at very low ion energies in combination with Monte Carlo simulations for several material systems [19–21]. Depending on the atomic number of the material of interest, slight modifications of the approach, i.e. the use of marker layers can be employed [22, 23]. Studies of compound materials are, however, so far limited, and thorough characterisation of the thin layers is required for more reactive systems of interest [19, 24]. Recently, sputter-deposited thin films of approximately 33–1160 nm thickness from EUROFER97 have been produced and characterised using different ion beam analysis (IBA) and microscopy techniques as well as mechanical tests [25] demonstrating the possibility of near-stoichiometric transfers and films with low levels of light bulk contaminants.

Based on that work, here, we have sputter-deposited ultrathin film stacks from EUROFER97 on an ultrathin layer of tungsten on Si. These films have been subsequently characterized and employed to demonstrate the feasibility of an approach of providing accurate and precise experimental reference electronic stopping cross-sections (SCS, $\epsilon$) of EUROFER97 for slow He and deuteron ions. We employed different ion beam analysis techniques for composition analysis of the resulting thin film stacks. Structural characterisation of the ultrathin films’ surface, volume and interface regions is performed using atomic force and transmission electron microscopy (AFM and TEM). Time-of-flight low-energy ion scattering (ToF-LEIS) was employed for stopping cross-section measurements of the resulting model films.

2. Methods

2.1. Sample preparation and characterisation

The samples were deposited using a magnetron sputtering system custom-designed by PreVac equipped with four MS2 63C1 magnetron sources compatible with targets of 50.8 mm (2 in.) diameter and 1–6 mm thickness. A 3 mm thick tungsten target and a 1 mm thick EUROFER97 target were used to synthesize sputter-deposited thin films of EUROFER97 on tungsten on silicon and carbon substrates. Due to the ferromagnetic characteristic of EUROFER97, the thickness of its target had to be minimized to 1 mm to alleviate interference with the required magnetic field of the magnetron cathode to maintain the argon plasma [25, 26]. The typical distance between the sputtering target and the substrate in this system is about 15 cm and is adjustable by ±2.5 cm. The system is capable of producing uniform films with a maximum nominal circular area of 50.8 mm (2 in.) in diameter when continuously rotating the substrate. Two batches of samples, each consisting of several samples, were prepared for this work with a difference in the sputter-deposited film of EUROFER97 thickness. Batch number 1 was deposited aiming for a nominal 7.5 nm sputter-deposited film of EUROFER97 on a 10 nm W film on Si substrates, and batch number 2 aimed for a nominal 12.5 nm sputter-deposited film of EUROFER97 on a 10 nm W film on Si substrates. For both batches, the substrates had a size of 10 × 10 mm² and were treated with isopropanol in the ultrasonic bath for 10 min before being transferred to the load lock of the sputtering system. The (100) Si substrates were primarily cleaned by the Radio Corporation of America (RCA) method [27] and dipped in hydrofluoric acid (HF), and the glassy C substrates were polished to a nominal average roughness of less than 50 nm. All the depositions were performed at room temperature with a base pressure of approximately $3 \times 10^{-7}$ mbar in the deposition chamber. The employed Ar atmosphere had a pressure of $5.6 \times 10^{-3}$ mbar with a gas flow rate of 10 standard cubic centimeters per minute (scm) using a DC power of 50 W. The substrates were rotated with an angular frequency of $10^2$ s⁻¹ during deposition to increase the uniformity of the produced films. To remove contaminants from the target surface, pre-sputtering was done against a shutter for 1–2 min before each deposition. The deposition rates were estimated to be $5.64 \text{ nm min}^{-1}$ by a Quartz Crystal Microbalance (QCM) in the system taking the nominal density of tungsten, and $4.2 \text{ nm min}^{-1}$ considering the nominal density of iron as the major constituent of EUROFER97. The W and EUROFER97 depositions were performed sequentially without exposition to air to minimize the presence of contaminants in the produced samples.
The composition of the produced films was characterized by Rutherford Backscattering Spectrometry (RBS) and particle-induced x-ray emission (PIXE) using 2 MeV He\(^+\) ions at the 5 MV pelletron tandem accelerator at the Tandem Laboratory of Uppsala University [28]. These measurements were performed simultaneously utilizing a passivated implanted planar silicon (PIPS) detector at a scattering angle of 170° for RBS, and a silicon drift detector (SDD) covered with a 79.5 μm mylar for PIXE. To improve mass separation between Fe and Cr, additional RBS measurement using 10 MeV \(^{12}\)C\(^{3+}\) ions was employed. The RBS spectra were analysed by SIMNRA code [29].

The structure of the films was examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM) at Uppsala University. TEM lamellae were prepared by Zeiss FIB/SEM Crossbeam 550 with a Ga Ion-Sculptor gun system. The areas selected as the regions of interest of the films were covered with a thin layer of platinum (Pt) to avoid being damaged by the Ga ions. TEM analysis was conducted with an FEI Titan Themis 200 system at an acceleration voltage of 200 kV. The surface of the samples was examined by PSIA XE-150 AFM in contact mode. The data was collected using PSIA XEP Basic software and images were further processed using Gwyddion software [30].

2.2. Charge-integrated low-energy ion scattering

For one sample from batch number 2 featuring a thicker layer of EUROFER97 on W on a Si substrate (denoted here as EUROFER97/W/Si), we recorded charge-integrated spectra by ToF-LEIS at the Tandem Laboratory, Uppsala University (ACOLISSA [31]). Being similar in its basic principles to RBS, this method enables composition depth profiling averaging over the beam spot area and thus being complementary to TEM. Therefore, similar to RBS, in combination with TEM, it enables an assessment of the thin film density. Finally, the obtained spectra can, together with computer simulations, be employed to demonstrate the suitability for extracting data on the electronic stopping cross-sections. The employed ToF-LEIS setup is capable of providing primary ion beams within the energy range of 0.5–10 keV out of gaseous sources like H, D, He and Ne, as well as molecular beams such as H\(_2\) and D\(_2\). The backscattered particles are detected by a set of two microchannel plates in a chevron stack configuration at a fixed central angle of 129° covering a solid angle of \(2 \times 10^{-4}\) sr The recorded charge-integrated spectra are subsequently converted to the energy domain. The system provides a high depth resolution in the monolayer regime [32] and has been earlier employed for obtaining electronic stopping powers from the energy width of spectra in backscattering geometry [21, 33] as well as the intensity of charge normalized backscattering spectra [33, 34].

After \textit{ex situ} deposition, the sample was loaded into the preparation chamber of the ToF-LEIS system together with bulk tungsten with a thickness of ca. 0.05 mm from Plansee (denoted here as W-Ref). Subsequently, Auger Electron Spectroscopy (AES) was used to assess the surface contaminants on both samples followed by sputter cleaning using a 3 keV Ar\(^+\) beam at an angle of 30° with respect to the surface normal with an average fluence of \(2 \times 10^{13}\) mm\(^{-2}\) on EUROFER97/W/Si sample and \(3.4 \times 10^{13}\) mm\(^{-2}\) on W-Ref. The employed low-fluence of ions in the Ar sputter cleaning is expected to have only minimum influence on the thin film areal density but is effectively removing surface contaminants. AES measurements after sputter cleaning on both samples showed a significant reduction in the amount of carbon and oxygen as the surface contaminants. The samples were transferred \textit{in situ} to the scattering chamber with a base pressure of approximately \(9 \times 10^{-10}\) mbar, without undergoing further treatment to ensure maintaining the total areal density, particularly, in the EUROFER97/W/Si sample as it is a key parameter in the data analysis and simulations of these experiments (more details in 3.3).

Primary 10 keV He\(^+\) ions and 8 keV D\(^+\) ions were employed to measure the ToF-LEIS spectra of the EUROFER97/W/Si sample in comparison to the bulk W-Ref while maintaining the same experimental conditions for both samples. For a quantitative evaluation of the energy loss in the sputter-deposited film of EUROFER97, the energy-converted ToF-LEIS spectra are compared to their respective Monte Carlo simulations using the TRim for BackScattering ions (TRBS) code [35]. These simulations account for multiple and plural scattering contributions. We employed the Thomas-Fermi-Molière potential with the Firsov screening length model. More details are discussed in 3.3. EUROFER97 is a complex multicomponent system; particularly the first nanometers of its surface can be altered in composition and morphology by ion irradiation and temperature elevation, with segregation of S, Cr and W observed for bulk samples [36]. Hence, it is advantageous to measure ToF-LEIS spectra on bulk W-Ref under the same experimental conditions to have an additional simpler system to ensure the best energy-conversion parameters for both samples.
3. Results and discussion

3.1. Composition

Figure 1(a) shows an RBS spectrum employing 2 MeV He\(^+\) primary ions recorded for EUROFER97/W/Si, i.e. the sample used in the ToF-LEIS measurements. Fe, Cr and W are observed along with Si. No signal of other species, e.g. S is detected. However, the peaks originating due to Fe and Cr are not clearly resolved (magnified in the figure inset). The SIMNRA simulation indicates an atomic composition of 11% Cr, 0.3% W and 88.7% Fe which agrees with the previous measurements on thicker sputter-deposited films from EUROFER97 \cite{25} and the nominal bulk composition of 9.5% Cr, 0.33% W and ca. 90.17% Fe \cite{3}. Moreover, the SIMNRA simulation provides the areal densities of the sputter-deposited film of EUROFER97 and the W layer which are used as input parameters in the TRBS simulations. Figure 1(b) presents the RBS spectrum from the same sample using 10 MeV\(^{12}\)C\(^{3+}\) projectiles. Carbon ions provide a better mass resolution to separate Fe and Cr peaks in the spectrum as it is more visible in the figure inset. The two most abundant isotopes of Fe, \(^{54}\)Fe and \(^{56}\)Fe, are also resolved in this case. In the SIMNRA simulation of figure 1(b), the obtained atomic composition from figure 1(a) is employed with minor modification in the Fe and Cr amount (89.2 ± 3% Fe and 10.5 ± 4% Cr).

An oxygen signal is not detectable in any of these RBS spectra due to the presence of the Si substrate signal. To be able to detect an oxygen signal in the Si plateau and observe a noticeable shift in the energy position of Si, Fe and W signals in the SIMNRA simulation, \(6.6 \times 10^{15}\) at/cm\(^2\) equivalent to ca. 34% O in the sputter-deposited film of EUROFER97 is needed, given the standard error (2\(\sigma\)) of the experiment in the energy interval expected to observe the oxygen signal. This limitation is due to the poor sensitivity of RBS to oxygen when a bulk of a heavier element is present in the sample. As O, however, is drastically reduced in the AES spectra after low-fluence Ar-sputtering, significant oxidation of the films can be excluded.

The PIXE spectrum shown in figure 2 recorded for the EUROFER97/W/Si, the sample used in the ToF-LEIS measurements, employing a primary beam of 2 MeV He\(^+\) confirms the presence of Fe, Cr, W and Si as well as Ta as a residual element and S and Ar as minor contaminants from EUROFER97 bulk and sputtering deposition, respectively.

3.2. Structure

For the structural characterization, samples from batch number 1 featuring a slightly thinner sputter-deposited film of EUROFER97 were used as they should be more susceptible to oxidation and inhomogeneous surface morphology than the samples from batch number 2 due to their shorter deposition time, and therefore, their thickness. Figure 3 shows a high-resolution-TEM (HR-TEM) image of an approximately 8.15 nm sputter-deposited film of EUROFER97 on a 12.45 nm W film on a Si substrate. The thicknesses were measured on an image taken by the scanning-TEM (STEM) where the interfaces are more distinguishable, thus providing a more precise thickness measurement. It is observed that the interfaces between different layers of the sample are reasonably uniform without significant intermixing of layers. No clear structure as in \cite{25} is observed for these samples. Taking the stack layer thicknesses from TEM together with the areal densities obtained from SIMNRA simulation of 2 MeV He\(^+\) RBS spectrum, the density of sputter-deposited films of EUROFER97 and W are inferred as 8.1 g cm\(^{-3}\) (about 3% higher than nominal EUROFER97 bulk density of 7.846 g cm\(^{-3}\)), and 16.7 g cm\(^{-3}\) (about 13% lower than W bulk density of 19.29 g cm\(^{-3}\)), respectively. The inferred density for the
deposited film thus agrees with the expected bulk value within the uncertainties, further confirming the high quality of the film.

Figure 4 displays an AFM image of the surface of a sample from batch number 1 with a thinner sputter-deposited film of EUROFER97. The covered area in this image is $2.164 \times 2.164 \, \mu \text{m}^2$, revealing a root mean square roughness of 217.7 pm. For comparison, a root mean square roughness of 7.8 nm has been reported for approx. 800 nm films sputter-deposited from EUROFER97 on a MgO substrate \cite{25}. The smooth surface of the present films ensures the possibility of obtaining accurate information from ToF-LEIS experiments, i.e. less uncertainty entering the ToF-LEIS spectra analysis due to the surface roughness of the sample affecting the path length and flight time of backscattered ions.

3.3. Stopping cross-section

Figure 5 presents the energy-converted ToF-LEIS spectra for 10 keV He$^+$ on the EUROFER97/W/Si sample and on the bulk W-Ref in black and red line $+$ symbol, respectively. The black solid line represents the most compatible TRBS simulation using an optimum corrected $\varepsilon$ for the sputter-deposited film of EUROFER97 as well as using the recently measured stopping cross-section of W ($\varepsilon_W$) at Uppsala University (Shams-Latifi 2023) \cite{8} for the W layer. The two black dashed lines represent TRBS simulations using $\pm 10\% \varepsilon$ of EUROFER97 exhibiting the sensitivity of the position of the W signal to the SCS of EUROFER97. The red solid line indicates
the TRBS simulation in bulk W-Ref using Shams-Lati 2023 $\varepsilon_W$ for He ions compared to the blue solid line using SRIM $\varepsilon_W$ [15] which underestimates $\varepsilon_W$ for He for energies below 8.5 keV.

Figure 6 shows the energy-converted ToF-LEIS spectra for 8 keV D$^+$ on the EUROFER97/W/Si sample and on the bulk W-Ref in black and pink line + symbol, respectively. The black solid line is the TRBS simulation for the EUROFER97/W/Si sample using an optimum corrected $\varepsilon$ for the sputter-deposited film of EUROFER97 as well as using Shams-Lati 2023 $\varepsilon_W$ [8] for the W layer. The two black dashed lines represent TRBS simulations using $\pm 10\% \varepsilon$ for EUROFER97 demonstrating the sensitivity of the position of the W signal to the SCS of EUROFER97. The pink solid line represents the TRBS simulation in bulk W-Ref using Shams-Lati 2023 $\varepsilon_W$ [8] for deuterons. In both figures 5 and 6, the arrows labelled as KE$_{0,W}$ and KE$_{0,\text{Fe}}$ mark the expected energy of a primary ion with the respective initial energy elastically scattered from a W and an Fe atom in a scattering angle of 129°, respectively. Here, K stands for the kinematic factor and E$_0$ denotes the initial energy. The arrow labelled as W$_\text{inter}$ indicates the position of the W signal originating from the interface between the sputter-deposited film of EUROFER97 and the W film.

Due to the presence of the sputter-deposited film of EUROFER97, the W signal from EUROFER97/W/Si is shifted towards lower energies compared to the W signal coming from W-Ref (figures 5 and 6). The incoming...
projectiles lose energy in the sputter-deposited film of EUROFER97 before reaching the W layer. Thus, from the corresponding TRBS simulations, one can extract the energy loss of the projectiles in the sputter-deposited film of EUROFER97. It is worth mentioning that the excellent fit to the Fe/Cr plateau together with the W-edge further excludes any significant oxidation of the sputter-deposited films stack. Additionally, it shows the sputter-deposited films are very homogeneous in composition. As a result of the present spectra, the electronic stopping powers of the deposited EUROFER97 model film for primary 10 keV He$^+$ and 8 keV D$^+$ ions according to their corresponding TRBS simulations in figures 5 and 6 are 10.57 eV/Å and 6.23 eV/Å assuming bulk density, respectively. These values correspond to stopping cross sections of 12.51 and 7.38 eV/(10^{15} \text{ atoms/cm}^2), respectively. The deduced stopping cross-section for 10 keV He$^+$ is thus found 10% higher than the predictions by SRIM using Bragg’s rule of stopping power additivity, while for 8 keV D$^+$, no correction for the SCS of sputter-deposited film of EUROFER97 was needed.

Note, that the present approach is different from the marker shift employed for determining the stopping cross-sections of ultrathin films of aluminium on tantalum taken in [22]. In the present approach, the stopping cross-section of EUROFER97 is accessible from both the spectrum height of the recorded signal of the film itself [37] as well as from the shift of the spectrum. From the excellent agreement of both spectral intensities and shifts of the W-edge, the equivalence of deduced data for the present energies can be shown.

4. Summary

Ion beam analysis and microscopy techniques were employed to characterise the composition and structure of sputter-deposited ultrathin films from EUROFER97 on an ultrathin layer of W on a Si substrate. A near-stoichiometric transfer was observed together with excellent interface and surface quality and a density of 8.1 g cm$^{-3}$, close to the expected bulk value. The films were subsequently studied using time-of-flight low-energy ion scattering (ToF-LEIS), further confirming the excellent quality, a homogeneous depth profile and their usefulness to experimentally deduce the electronic stopping cross-section of EUROFER97 for primary 10 keV He$^+$ and 8 keV D$^+$ ions by comparison to Monte Carlo simulations using the TRBS code. The resulting stopping cross-sections are comparable to predictions by SRIM for EUROFER97 bulk using Bragg’s rule of stopping power additivity.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

CRediT authorship contribution statement

Jila Shams-Latiﬁ: Investigation, Methodology, Formal analysis, Validation, Software, Data curation, Writing - original draft, Writing - review & editing, Visualization. Eduardo Pitthan: Conceptualization, Methodology, Investigation, Data curation, Writing - review & editing, Supervision, Project administration. Tuan Thien Tran: Investigation, Writing - review & editing. Rajdeep Kaur: Investigation, Writing - review & editing. Daniel Primetzhofer: Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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