RUTHERFORD BACKSCATTERING FOR EVALUATION OF POROSITY DISTRIBUTION IN THIN BLACK SILVER FILM

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Abstract

The determination of porosity in thin, highly porous films is essential for many technological applications. For evaluating the porosity of materials, various methods have been developed. In this study, Rutherford Backscattering was used to analyze a thin layer of black silver at several angles of the probing beam. Through careful simulation of the energy spectra using a MC SIMNRA code, depth profiles of the constituent atoms were determined, enabling the quantification of both the total and directional relative occupancy of Ag in the layer. This provided a new (albeit simplified) perspective on the porous structures, allowing for the evaluation of Ag porosity distribution within the layer. The samples were prepared at the University of Chemistry and Technology in Prague (UCT Prague) by evaporating silver in an Ar ambient atmosphere, while the RBS analyses were conducted at the Tandetron accelerator at the Nuclear Physics Institute in Řež using a 2 MeV alpha particle beam.

Keywords: Black silver, porosity, Rutherford Backscattering, inclination angles, Energy storage systems, ion beam modifications, nanofilms

1. INTRODUCTION

Porosity is a critical parameter of functional materials that needs to be determined as accurately as possible, especially for thin films, where it significantly influences their physical, chemical, and electrical properties [1]. This, in turn, directly impacts their potential technological applications. A higher degree of porosity increases the interactive surface area, which is particularly important in fields such as gas sensing (where a high surface area enhances reactivity) [2], catalytic converters [3], the efficiency of supercapacitors (due to improved charge storage) [4], micro-nanoelectronics (by reducing electrical delays in integrated circuits) [5], and thermal conductivity (e.g., in insulating layers) [6].

However, increased porosity can also compromise the mechanical and corrosion resistance of the layers (as high porosity reduces strength, structural integrity, and resistance to corrosion in aggressive environments), thus negatively affecting their potential usability. Therefore, accurately determining porosity is crucial for optimizing the preparation of thin porous films and achieving their desired functionality.

There are various techniques for evaluating the porosity of thin films tailored for different applications (e.g., ellipsometric porosimetry, positron annihilation spectroscopy, grazing incidence small-angle X-ray scattering) [7]. In this study, the nuclear analytical technique of Rutherford Backscattering (RBS) [8] was used to investigate the porosity of a thin layer of black silver (B_{Ag}) [9]. RBS, which involves the interaction of a probing beam with atoms in the sample, allows for detailed composition and profile measurements. However, to obtain relevant results, the method requires certain conditions: low surface roughness (< 5 - 10 nm to maintain a welldefined scattering angle for energy analysis), high flatness (to ensure uniform irradiation of the sample), a clean surface (to prevent artifact formation), and a thickness of less than 1000 nm (to maintain high depth resolution - while thicker samples can be analyzed, depth resolution decreases due to ion straggling). In the case of porous structures, achieving low roughness and high flatness is particularly challenging. Nevertheless, despite these limitations, RBS can still provide valuable data that is difficult to obtain with other techniques.

In this study, the porous structure of B_{Ag} was irradiated at several selected angles. The aim was to measure the energy spectra despite the aforementioned limitations and observe how they vary with different probe beam inclinations. It was assumed that the relative distribution of silver atoms in the layer (or, alternatively, their relative occupancy) changes with depth, influenced by the formation process of B_{Ag}. Through detailed analysis of the spectra, it is possible - despite simplifications - to trace the relative occupation of silver in the sample as a function of depth, thereby determining the porosity of the layer and its depth profile as a reciprocal value. This work presents the initial results from the analysis of porous B_{Ag} using the RBS method at different probe beam inclinations.

2. METHODOLOGY

Thin films of black silver were prepared using the thermal evaporation technique at the University of Chemical Technology in Prague [10]. Si wafer slips (5x5 mm) were used as substrates, which were cleaned in a standard manner using an ultrasonic bath with isopropyl alcohol. For deposition, the substrates were fixed onto a sample holder (a metallic plate with masks), positioned approximately 20 cm from the silver (Ag) source. Prior to deposition, the chamber was evacuated to a base pressure of 4×10^{-4} Pa, and for deposition, 100 Pa of high-purity argon (Ar) was introduced into the chamber. A molybdenum (Mo) crucible was used as the evaporation boat, and a DC power supply (KXN-15200D) was employed for the process. For deposition, 99.99% pure silver (Ag) wire was used in a single evaporation step, lasting about 30 seconds, with a top heating current of approximately 70 A.

The porosity of the B_{Ag} layers was analyzed by the Rutherford backscattering (RBS), applied at various angles of ion incidence (2 MeV alpha particles). For each measured spectrum, a MC simulation was performed using the SIMNRA code [11] to determine the silver occupancy and its distribution along a given direction. This approach enabled profiling of the porosity in the thin black silver films - information that is otherwise difficult to obtain using other analytical methods.

The measurements were conducted within the CANAM infrastructure at the Nuclear Physics Institute (NPI) using a Tandetron 4130 MC accelerator [8]. RBS was performed with 2 MeV alpha particles at several angles of inclination: 0° (normal incidence), 10°, 20°, 30°, 40°, and 50°. The ion beam, with a cross-sectional size of a few millimeters, was directed at the center of the sample. To achieve the desired beam inclination, the sample (fixed on a substrate holder) was rotated along its axis. Each RBS measurement was performed under consistent conditions—using the same beam current (~10 nA) and ion fluence (~5 mC).

3. RESULTS

Figure 1 shows the RBS spectra of porous B_{Ag} layers measured at different inclination angles, alongside the simulated spectra for a full (non-porous) Ag film with the same atomic content as determined from the measured RBS data. Both the measured and simulated spectra exhibit similar trends, but also distinct differences. As the inclination angle increases, both spectra nominally increase and broaden. However, the experimental spectra become asymmetric, in contrast to the simulated data, with the left side expanding toward lower energies. This asymmetry arises from the interaction of the probing beam with a larger number of atoms compared to an ideal full sample with uniform thickness. It is important to note that for simplicity, effects such as probe beam divergence, multiple scattering, Ag oxidation, and others - which also influence the measured RBS spectra - are neglected in this analysis.

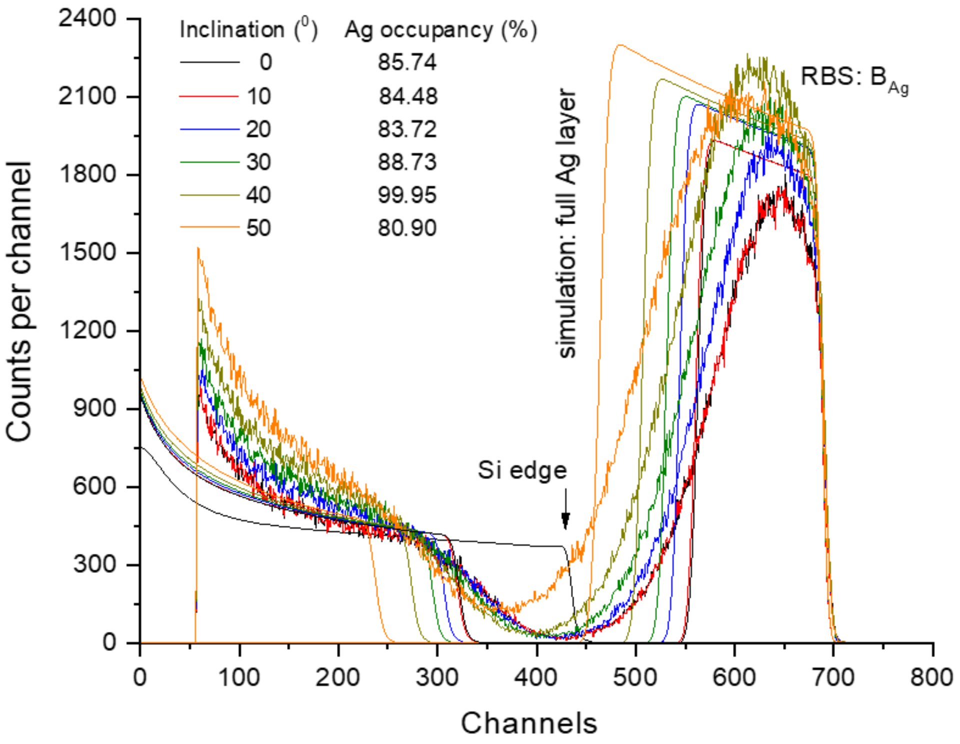

Figure 1 RBS spectra of black silver (B_{Ag}) measured for different angles (0˚, 10˚, 20˚, 30˚, 40˚, 50˚) of inclination of the incident 2 MeV alpha particles, and corresponding simulations of RBS spectra evaluated for an ideal full Ag layer containing the same number of atoms as the measured spectra. The porosity of B_{Ag} is given for different inclination and is based on the ratio of measured and theoretical RBS spectra.

For normal incidence (where the probing ions impinge the surface at 90˚), the B_{Ag} structure consists of tall, narrow nanodomains (with variable length and width) through which the probe ions pass. As the ions lose energy, they register in the spectrum at lower energies. By comparing the experimental data for the porous layer with simulated spectra for a full layer containing the same number of atoms, one can estimate the portion of the RBS spectra that overlaps with the simulated spectra, as well as the portion that deviates from the simulation. The deviation corresponds to the Ag atoms in nanodomains above the thickness of the full layer.

In other words, by comparing the real RBS spectra of the porous layer with the RBS simulations for a full layer with identical atomic content, it is possible to estimate the degree of porosity within the thickness of the full layer. (Note that some effects that could influence the measured data are, for simplicity, ignored – see later.) **Figure 1** shows the Ag occupancy data values, determined for each inclination angle, indicating that silver, at the assumed full-layer thickness (corresponding to 1221×10^{15} atoms/cm^2 in the normal direction), would occupy at least 80% of the space. However, this result represents an upper limit of occupancy, as it does not account for the lower density of porous Ag compared to the full layer.

Simulating the actual spectrum allows for determining the depth distribution of Ag - its relative concentration - and consequently relative occupancy, which reflects the porosity.

An interesting perspective emerges from the RBS measurements at different inclination angles. As the angle of inclination increases, ions interact with more nanodomains, forming the layer more densely. The measured spectra then provide greater detail of the porous structure, revealing the variability in the layer's porosity, which becomes particularly apparent at higher angles of inclination. Similar to the normal incidence, larger inclination angles also allow for estimating the degree of occupancy (porosity) and its progression (profile) in the given direction.

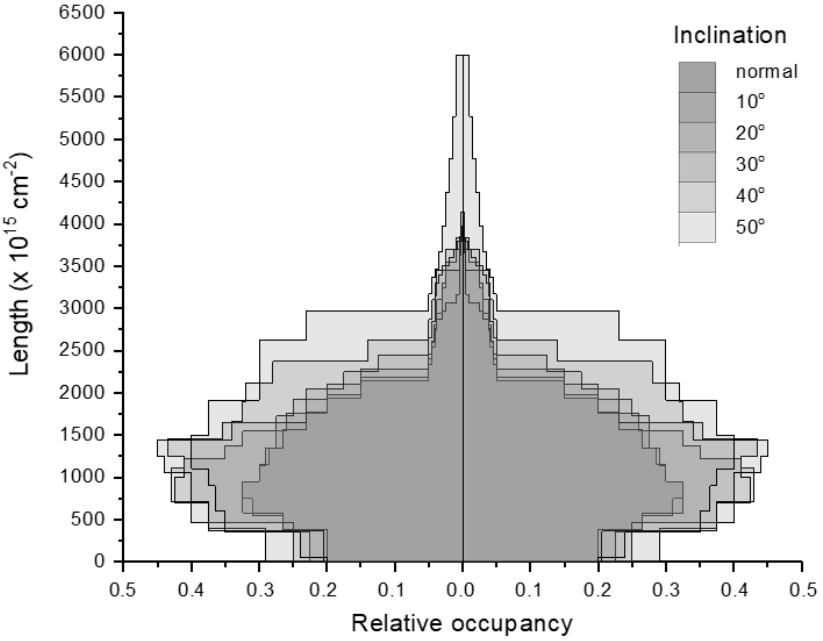

Figure 2 Dependence of the length of porous structures (in units of 10^{15} at. cm^{-2}) on their occupancy. The data are derived from RBS measurements and their simulation using SIMNRA.

Figure 2 shows, for each inclination angle, the structure representing the distribution of nanodomain sizes and their corresponding Ag occupancy in the layer along the given direction. The shape of these structures is derived from the RBS spectrum simulations measured at the corresponding angles (**Figure 1**) and represents the relative depth profiles of Ag. It is evident from **Figure 2** that the nanodomains exhibit a dome-like shape, with an expansion (corresponding to up to 0.9 relative occupancy) for sizes in the range of (800 – 1300) x 10^{15} at. cm^{-2} and a narrow stalk (0.1 – 0.5) x 10^{15} at. cm^{-2}. The dome shape gradually changes with inclination angle, steadily increasing and expanding.

From the relative occupancy distribution shown, the porosity distribution can be easily determined, i.e., the porosity size at each depth. For instance, as seen in **Figure 2**, for normal incidence (0°), the occupancy of structures smaller than 500 x 10^{15} at. cm^{-2} is about 40%. A sharp increase in occupancy is then observed, peaking at around 65% for structures with a height of 750 × 10^{15} atoms/cm². As the nanodomains grow in size, occupancy decreases to approximately 30% when their height reaches about 2200 x 10^{15} at. cm^{-2}. The stalk of the dome is formed by features with heights up to about 4000 x 10^{15} at. cm^{-2} and widths (occupancy) of approximately 8%.

The structures, evaluated for each angle, show the dependence of nanodomain size on relative occupancy. As seen, this dependence changes with the angle: for each nanopillar size, occupancy increases, and the stalk of the domes grows. This trend is expected, as with increasing inclination angle, individual aspects of the dome structure become more pronounced. At sharper angles, the thicker parts expand more, and the taller parts increase in size even further.

4. CONCLUSION

An analysis was conducted to assess the porosity of a thin layer of black silver, composed of nanodomains on a Si substrate, prepared using resistance-heating evaporation in an Ag atmosphere. Rutherford Backscattering Spectrometry (RBS) was used, employing 2 MeV alpha particles to irradiate the porous layer at several selected angles. These angles facilitated the investigation of the Ag layer in specific directions and allowed for tracking how the energy spectra change, reflecting variations in the porous nanostructure.

The measured spectra were carefully simulated, and, based on detailed depth profiles of the constituent elements (Ag, Si, and O – the latter due to silver oxidation), specific dependencies were established between the size of the Ag nanodomains and their frequency of occurrence (occupancy level). This data enabled not only the assessment of the overall Ag occupancy in the layer (which is inversely related to its porosity), but also the distribution of occupancy (or porosity) along the selected irradiation directions.

However, it is important to note that certain drawbacks, such as high surface roughness and low flatness, were neglected in the simulation, which may influence the obtained results. Despite these simplifications of the complex ion backscattering process, this approach still provides valuable insights into the porosity parameters of black metals, which are otherwise difficult to determine.

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