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X-ray elastic constants determined by the combination of $\sin^2 \psi$ and substrate-curvature methods

Dedicated to Professor Dr. Dr. h. c. Hein Peter Stüwe on the occasion of his 75th birthday

A new methodology is presented that allows the quantification of experimental X-ray elastic constants of polycrystalline thin films without use of special diffractometer attachments. The approach is based on the combination of $\sin^2 \psi$ and curvature methods. The elastic strains in the polycrystalline films are characterized by the measurement of lattice spacings at different sample tilt angles, while the macroscopic stress in the film is calculated from the substrate curvature applying the Stoney formula. The radius of the curvature is determined from a sequence of rocking curves measured at different sample positions. The method is demonstrated on Al thin films deposited on Si(100) substrates. The X-ray diffraction measurements were performed at the synchrotron source BESSY in Berlin.

Keywords: X-ray diffraction; Synchrotron; Stress; Thin film; Aluminium

1. Introduction

Residual stresses in thin films influence decisively the structural integrity and the performance of various kinds of devices [1]. In order to calculate the residual stresses in polycrystalline thin films from the diffraction data, X-ray elastic constants (XECs) are used [2]. The magnitude of XECs is influenced by the film material, the anisotropy, the elastic interaction between grains and the reflection measured [3]. In practice, XECs can be calculated from theoretical models taking into account single-crystal elastic constants, texture, and elastic interaction between grains [4]. The application of the theoretical models is usually very laborious, especially in the case of textured films where the orientation distribution function must be considered [3, 4]. Alternatively, XECs can be determined experimentally applying diffraction techniques [5]. The thin film structures are in situ mechanically loaded, and the strain changes are monitored by in-situ diffraction as a function of the applied load [5]. In this case, special attachments must be employed to mechanically test the films in the diffractometer in a controllable way.

The main aim of this paper is to introduce a new self-consistent diffraction technique which can be used to determine XECs experimentally without the use of special diffractometer attachments. The method, based on the combination of $\sin^2 \psi$ and curvature methods, is demonstrated on Al thin films deposited on Si(100) substrates.

2. Experiment

Al thin films were deposited on Si(100) substrates by balanced magnetron sputtering, using an aluminium target (99.5 % Al) in argon atmosphere at room temperature. Prior to the deposition, the substrates were cleaned ultrasonically in acetone and alcohol. Additionally, ion etching was applied to remove contaminants from the silicon surfaces. Samples with various film and substrate thickness were prepared, as listed in Table 1. After the deposition process, the samples were annealed in vacuum at 450°C for 15 minutes in order to increase the stress magnitude in the films [6].

The samples were 5 mm wide and differed in length between 7 and 17 mm. The rectangular samples were glued just with one of their narrower sides on sample holders to allow the bending caused by balanced mechanical moments between the film and the substrate. To eliminate alignment errors when characterizing strains in the films, Si powder with a mean grain size of about 1.5 \(\mu\)m was spread on the film surface and served as an internal standard when evaluating the lattice spacing from the diffraction data.

The structural properties of the samples were characterized using X-ray diffraction (XRD) at the KMC2 beamline of BESSY synchrotron facility in Berlin, Germany. The KMC2 beamline is equipped with a double-crystal silicon monochromator and a focusing mirror which provide \(10^9\) photons per second at the sample. The beam wave-
Table 1. Basic parameters of Al/Si(100) structures. The thin films and the substrates possessed different thickness $h_t$ and $h_s$, respectively. From the XRD measurements, the radius of curvature $R$, the unstressed lattice parameter $d_o$, and the slopes of $\sin^2 \psi$ plots $\partial d_{\psi}^{\text{hkl}} / \partial \sin^2 \psi$ were determined. The macroscopic stress $\sigma_{11}$ and the XECs $s_1^{11}$ and $s_2^{11}$ were calculated.

<table>
<thead>
<tr>
<th>$h_t$ (nm)</th>
<th>$h_s$ (mm)</th>
<th>$R$ (m)</th>
<th>$\sigma_{11}$ (MPa)</th>
<th>$d_o$ (pm)</th>
<th>$s_1^{11}$ (10^{-11} Pa^{-1})</th>
<th>$s_2^{11}$ (10^{-11} Pa^{-1})</th>
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<td>1.94</td>
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</tbody>
</table>

length was set to 0.15406 nm. Samples were mounted onto a 6-circle Huber goniometer. The beam footprint on the sample during diffraction measurements was approximately $0.2 \times 0.5 \text{mm}^2$. The diffraction signal was collected using an area-sensitive multiwire proportional detector (Bruker AXS) mounted on the detector arm of a goniometer at a distance of 0.488 m from sample.

3. Methodology

X-ray diffraction (XRD) is routinely used to determine residual stresses in polycrystalline thin films [2 – 9]. For this purpose, the $\sin^2 \psi$ technique is usually applied [2]. By scanning $hkl$ reflections at selected sample orientations described by the angle $\psi$ (Fig. 1), the lattice spacing $d_{\psi}^{\text{hkl}}$ can be determined for different groups of crystallites possessing various orientations with respect to the sample normal [2]. It is supposed that, during a diffraction experiment, a sufficiently large volume is irradiated, providing a statistically representative information on the structural properties and mechanical behaviour of the polycrystalline film. In the case of in-plane isotropic films, the macroscopic volumearraged stress $\sigma_{11}$ can be calculated according to

$$d_{\psi}^{\text{hkl}} = d_o^{\text{hkl}} \left( 1 + \sigma_{11} \left[ 2 s_1^{\text{hkl}} + 1/2 s_2^{\text{hkl}} \sin^2 \psi \right] \right)$$

where $d_o^{\text{hkl}}$ represents the unstressed lattice spacing, $s_1^{\text{hkl}}$ and $s_2^{\text{hkl}}$ are XECs and $\psi$ represents the angle between the sample and the crystallographic plane $(hkl)$ normals (Fig. 1). Since

$$\frac{\partial d_{\psi}^{\text{hkl}}}{\partial \sin^2 \psi} = \frac{1}{2} d_o^{\text{hkl}} s_{11}^{\text{hkl}}$$

the macroscopic stress $\sigma_{11}$ can be calculated from the dependence of $d_{\psi}^{\text{hkl}}$ on $\sin^2 \psi$ applying correct $s_{11}^{\text{hkl}}$ and $d_o^{\text{hkl}}$ [2]. Conversely, applying known $d_{\psi}^{\text{hkl}}$, $\sigma_{11}$, and $d_o^{\text{hkl}}$, the values $s_1^{\text{hkl}}$ and $s_2^{\text{hkl}}$ can be calculated from Eqs. (1) and (2), respectively.

In this work, the macroscopic volume-averaged stress $\sigma_{11}$ is determined from the substrate-curvature measurements using the Stoney formula

$$\sigma_{11} = \frac{E}{6(1 - \nu)} \frac{h_t^2}{h_s} \frac{1}{R}$$

where $h_s$ and $h_t$ stands for substrate and film thickness, respectively, $R$ represents the radius of the curvature of the substrate, and the term $E/(1 - \nu)$ is the biaxial modulus of the substrate [10]. The approach based on the Stoney formula is widely applied, especially in the case of temperature-dependent studies of stresses in thin films, while the substrate curvature is usually determined by optical techniques [11].

In the present work, the curvature of the substrate was determined by diffraction, as schematically depicted in Fig. 2.
[7]. The 2D detector was moved to the calculated 2θ position corresponding to the Si 400 reflection. By rocking the samples around the ω axis (Fig. 2), the diffraction on Si(400) was observed. Subsequently, the sample was moved, using a linear stage in the beam of Δx distance, along its longer side, and the same rocking procedure was repeated. In this way the dependence of ω on x was obtained. To assess the radius R of the substrate curvature (Fig. 2)

\[ R = \frac{\Delta x}{2 \sin \left( \frac{\Delta \omega}{2} \right) } \]  

Applying the radius R of the curvature (Eqs. (3), (4)), it was possible to determine the macroscopic isotropic stress \( \sigma_{11} \) in the samples. Additionally, from the intercepts of the \( d_{\theta}^{\text{Al}} \) dependences on \( \sin^2 \psi \), the magnitude of \( d_{\theta}^{\text{Al}} \) was determined (Eq. (1)). The XECs \( s_{\text{Al}}^{1\text{kl}} \) and \( s_{\text{Al}}^{2\text{kl}} \) were then calculated for different films using Eqs. (1), (2).

4. Results and discussion

The diffraction patterns of Al thin films on Si were measured by a two-dimensional (2D) detector. The detector was moved to the 2θ position of 114° and, for each sample, the 2D data were collected for 180 seconds at different sample tilt angles ψ, applying the \( \Delta \sin^2 \psi \) step of 0.1 (Fig. 1). A typical diffraction pattern is presented in Fig. 3. The three vertical lines represent Al 331, Si 531, and Al 420 reflections. The Si 531 reflection originates from Si powder spread on the thin film surface (Fig. 3). For each measurement position ψ, the 2D data were integrated and 2θ positions of the peaks were determined by fitting. The Si 531 reflection was always considered as a reference supposing the lattice spacing \( d_{531} = 9.18 \text{ pm} \).

The sections of Debye–Scherrer rings in Fig. 3 corresponding to Al 331 and Al 420 reflections document that the Al thin film was not strongly textured. Also for other thin films, the Debye–Scherrer rings were always continuous with no maxima along the ring. Therefore, the Al films were considered as isotropic.

In Fig. 4, the Al lattice parameter \( a \) is plotted as a function of the sample tilt ψ for all samples investigated (Table 1). The actual magnitude of the Al lattice parameter in Fig. 3 was calculated from the 2θ positions of Al 331 reflections (Fig. 3). Figure 4 documents a presence of tensile stresses in the thin films. For each sample, the slope \( \partial d_{\theta}^{\text{Al}} / \partial \sin^2 \psi \) was fitted (Table 1). The intercept of the \( \sin^2 \psi \) plots from different samples yields the unstressed lattice parameter of Al \( a_{\text{Al}} = 404.99 \text{ pm} \).

Due to the relatively small aluminium Zener’s anisotropy ratio of 1.21, the slopes of \( \sin^2 \psi \) plots for Al 420 reflections were practically identical with those for Al 331 reflections. Therefore, the experimental data from Al 420 (Fig. 3) are here not considered, for reason of simplicity.

After the characterization of strains in Al thin films, the curvature of the samples was evaluated. The quantification of the curvature was performed by measuring rocking curves of very strong Si 400 reflections of the monocrystalline silicon substrate at different sample positions \( x \) (Fig. 2). At first, the 2D detector was moved to the Si 400 2θ position of 69.13 degrees. To protect the detector from a damage caused by the very strong signal from the substrate, a Cu attenuator was inserted into the primary beam. Then, for each \( x \) position, the sample was rotated around the ω axis (Fig. 2) and the integral intensity from the 2D de-
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The data from the sin² ψ method would be used to refine the unstressed lattice parameter \( d_0 \) (Fig. 4), while the curvature method would be used to quantify the macroscopic in-plane stress \( \sigma_{11} \) in the film (Fig. 5). Subsequently, by applying Eqs. (1), (2), the values \( s_{331}^{1} \) and \( s_{331}^{2} \) could be calculated.

In the present work, Al thin films with the thickness in the range of 0.4–3.2 μm were analysed. The results in Fig. 6 do not indicate any influence of the film thickness on XECs. In the future, it would be interesting to analyse the influence of the film thickness on the dependence of \( \partial d_{331}^{11}/\partial \sin^2 \psi \) on \( \sigma_{11} \). In the case of relatively thick films (with the thickness above 10 μm), the influence of strain gradient and near-surface strain relaxation should be taken into account. The most interesting will be to study films with a thickness below 100 nm in order to resolve the influence of the “size effect” on the magnitude of XECs.

The present work focused on the characterization of the single-phase thin films, while the macroscopic stresses (estimated from the curvature) were compared with the elastic strains measured using the sin² ψ technique. One can expect that in the case of thin films with more constituents, the phase-balanced stresses would influence the results and could make the calculated XECs invalid [14, 15]. In the case of films with more phases, the local stresses of the second and third order (corresponding to the measured elastic strains) can vary significantly and may differ from the average macroscopic stresses [14, 15]. Further, if the thin films under the study are highly anisotropic or have experienced plastic flow, the presence of the interaction stresses must be considered when calculating the XECs. The XECs calculated using the present approach are, therefore, dependent not only on the material but also on the thin film architecture and the thermal history. One of the main advantages is, however, that the XECs can be determined in a relatively simple and straightforward way.

5. Conclusions

A novel approach to determine X-ray elastic constants was presented. For this purpose, XRD was used to characterize elastic strains, using the sin² ψ method, and macroscopic stresses, using the curvature method, in polycrystalline Al thin films on Si(100). The results document that the magnitude of the in-plane elastic strain is proportional to the magnitude of the in-plane macroscopic stress. The experimental data were used to calculate XECs of the Al thin films. The main advantage of this approach resides in the fact that the experimental XECs can be determined without the use of in-situ loading diffraction attachments.

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