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Rietveld Texture and Stress Analysis of Thin Films by X-Ray Diffraction

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Abstract. In many applications where thin films are involved, like in electronics or ferroelectricity, it is required quantitatively to characterize their texture and residual stresses. Moreover, commonly the films contain several layers and phases, and due to the severe overlapping of the reflection peaks and sharp texture, the analysis of both features is difficult or even not possible by the traditional pole figure- and $\sin^2\psi$ -techniques. Rietveld texture and stress analysis is a viable methodology to overcome the overlapping problem and a dedicated system composed by a special diffractometer and software for the analysis has been developed to accomplish the task. The diffractometer is mainly composed by a goniometer with an open eulerian cradle coupled with a curved position sensitive detector covering 120° to collect a large part of the 2θ spectrum in a reasonable time. The data is then processed by the program MAUD for Rietveld Texture and Stress Analysis to obtain the ODF, the macrostress tensor and all information about crystal structure and microstructure of the phases present in the layered film structure. The method take into account the thickness of the films and the sequence of the layers as well as the phase fraction of the phases inside each layer. For the texture analysis inside the Rietveld, different approaches are available, from the simple March-Dollase formula to the conventional WIMV, up to a special version of WIMV for very sharp textures currently of interest in the electronic/ferroelectric field. This entire system has been tested and proved successfully for different cases and some analysis examples are presented to show the powerful combination of all these methodologies with a dedicated instrument quantitatively to analyze films of interest for the industry of ferroelectric and electronic appliances.

Introduction

Rietveld introduced the so-called Rietveld method on the aim to refine the crystal structure directly from a powder pattern instead of using integrated intensities [1]. Now the method has been evolved and this idea of fitting the pattern by refining some physical/crystallographic quantities is becoming more and more popular thanks to a general better accuracy of the results relying on a large amount of data.

Rietveld texture analysis [2-4] is now becoming a viable tool to analyze texture and has recently be applied successfully to both complex earth minerals [5-7] and composite materials [8]. Respect to the normal quantitative texture analysis where the ODF (Orientation Distribution Function) is obtained from a definite number of incomplete or complete pole figures, in Rietveld texture analysis the ODF is obtained from a certain number of full spectra. There are some advantages on that. Complex situations like low symmetric phase or polyphase samples with highly overlapped peaks can still be analyzed. Relying on a bigger number of peaks, a smaller coverage of the pole figure is needed. Finally, the texture analysis can be easily combined with other analyses to take mutual advantage.

The drawback of the analysis is that it requires a diffraction instrument to collect all the required spectra in a reasonable time and the normal texture instruments available in the laboratories out of the

big facilities are not suitable for that. Instead, in synchrotron and neutron facilities spectrometers with large position sensitive detectors or energy dispersive detectors can be easily found, and it has already demonstrated the feasibility of the analyses with such kind of equipment in neutron diffraction [5, 7, 8].

We aim to demonstrate as this kind of analysis is suitable also in normal laboratories using a special diffractometer and as this can be especially advantageous in the case of thin film analyses where X-ray diffraction is employed preferentially to Neutron diffraction.

Experimental

Two films have been measured. One is a 500 nm Aluminum thin film sputtered on a Silicon wafer, another is an SBT ($(Sr_{0.82}\text{-}Bi_{0.12})Bi_2Ta_2O_9$) film of around 300 nm over a Pt layer of 50 nm also on a Si wafer, but prepared by spin coating. All measurement has been done with a special instrument composed principally by an Eulerian cradle and a large position sensitive detector.

The incident beam is equipped with a multilayer to monochromatize the CuKα radiation and a cross slit system to adjust the beam spot. The goniometer can be moved in the ω or θ, χ and ϕ angles as well as for x, y and z position to adjust its position and alignment respect to the beam. The 120 degrees position sensitive detector is mounted on the 2θ motor. The multilayer provides a very small beam in the equatorial direction to be perfectly suited also for reflectivity and small-angle measurements.

An ad hoc program has been developed to control the goniometer and it is interfaced with the analysis software (Maud, see ref. [9]) through a client-server system that enables Maud to launch the measurements and retrieve the data on the internet. The analysis program can suggest the best conditions for the measurement to minimize collection time still retaining all the necessary informations based on preliminary data about the nature of the sample and analysis requested. Different texture models has been implemented in Maud from the classical harmonic method, to the WIMV [10] and its last modification E-WIMV to avoid the interpolations step in very sharp textures.

Discussion

The first analysis has been done on the Aluminum thin film. A starting quick measurement was performed on the sample with a standard grid of 5° x 5° steps in χ and ϕ to have an idea of the sharpness of the texture and of its sample symmetry. A very sharp texture was easily recognized, that would require a fine measurement grid. Also it showed a perfectly fiber texture along the axis perpendicular to the film major dimensions. As a consequence we choose to measure on a very fine grid of 1° in χ and to spin the sample around its fiber texture axis to avoid unnecessary wasted time in measuring along the ϕ angle. The analysis has been done with Maud assuming a two layers structure in which the substrate (Si wafer) is one layer with the Aluminum layer on top. Small spots of the Si wafer emerged at some angles in the measured spectra and so the Si wafer was also simulated imposing a fiber texture that was enforced by the spinning along ϕ during the measurement. Indeed the analysis would give the same results if the Si were neglected because its small peaks are very week and located far from the Al film peaks. Statistically they weighted nearly to nothing in the least squares fitting performed by the program to determine the texture and the physical characteristics of the Al film.

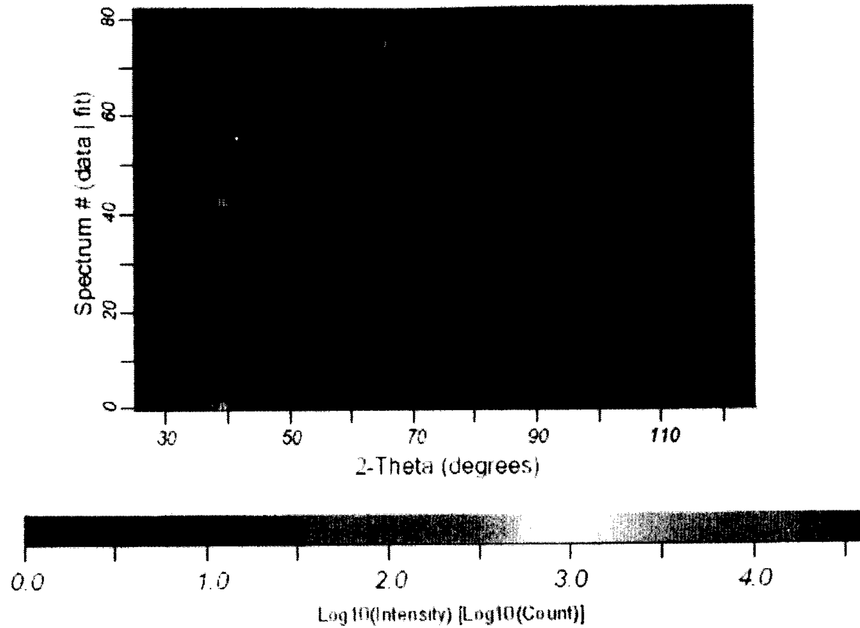

Fig. 1. 2D map of the intensity for the Al film analysis. The lower part contains the measured spectra and the upper part the calculated ones.

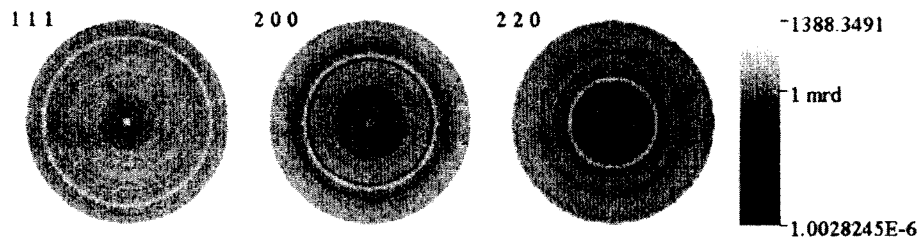

Fig. 2. Aluminum's reconstructed pole figures (log plot) from the fitting of the spectra of Fig. 1.

Figure 1 reports a 2-dimensional plot of the intensity along the 2θ and χ axes (the χ axis is substituted by the spectrum number increasing with the increasing angle from 0 to 40°). If the fitting is perfect the lower half (measured spectra) and the upper half (calculated spectra) of the map should coincide. The lower part is obviously noisy as it represents the measured intensity. A logarithm plot on the intensity is shown to emphasize the smaller peaks and especially the one due to the Si wafer. Curiously, in the measured part the spots at high χ are all inclined and this was recognized as due to the oval X-ray beam spot on the sample that inclines itself with the tilting in χ displacing the extremities from the correct position along the z-axis of the sample. The artifact is indeed visible only by the fact that the texture is very sharp giving rise to small spots, otherwise it wouldn't be recognizable. It is not possible to model this artifact in the Maud program, so the fitted spots are not inclined at all.

Figure 2 shows the reconstructed pole figure from the ODF as obtained from the analysis. It was necessary to use the E-WIMV method imposing a fiber texture and a 1° x 1° x 1° grid. Using a 5° x 5° x 5° cell or even a 2.5° x 2.5° x 2.5° cell grid was not sufficient to reproduce the sharp texture of the film. This can be view also as a good resolution of the instrument that is not broadening too much the

texture by the instrumental aberrations. The texture sharpness (F2, see ref. [10]) for the Aluminum phase is 11.31.

The second analysis has been done on the SBT film. The sample is composed of an SBT film on top of a Pt film deposited over a Si wafer previously coated by a SiO_2/TiO_2 layer too small to be visible under diffraction. Also the SBT and Pt films exhibit a fiber texture but much less sharp than the previous Al film. Instead, the major problem that prevents other texture tools to work well in this case is that the SBT phase is tetragonal with a lot of peaks, all overlapped, and no isolated peak of the Pt can be located also. So the Rietveld texture analysis was an obliged choice to perform the analysis.

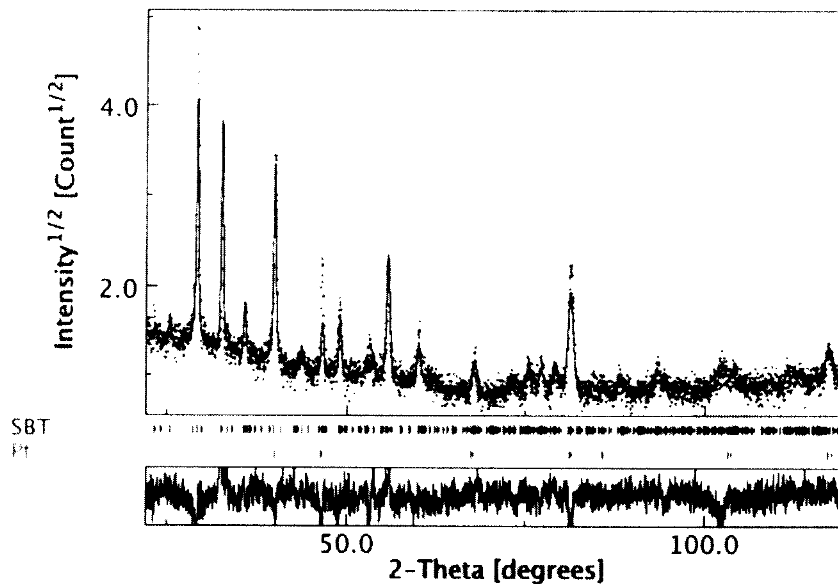

Fig. 3. Measured (dots) and fitted (line) spectrum for the SBT/Pt films by the Rietveld texture analysis.

Figure 3 reports a single plot of a diffraction spectrum as fitted by the program to show the peaks overlap and location. Figure 4 shows the 2-dimensional map equivalent to figure 1 for the SBT/Pt film. In this case the measurement was done on a 5° x 5° grid in ϕ and χ has there were some slight deviations from the fiber texture (see figure 5). Again the lower part consists of the measured spectra and the upper part of the fitted ones. The spectra are reported on the ordinate axis by progressive number and numbered following the convention: it starts with index 0 for $\chi = 0°$ and $\phi = 0°$ and then increases with ϕ up to 355°, then χ increases by 5° and another scan in ϕ follows and so on up to 25° in χ. The sample was quite small and so it was not possible to go higher than 25° in χ avoiding the beam out of the sample problem.

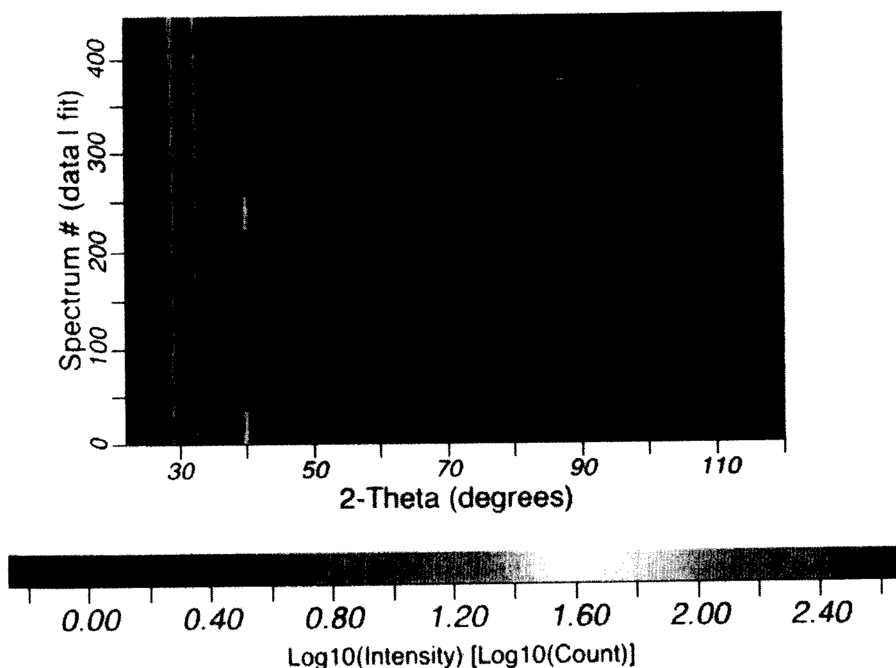

Fig. 4. 2D map of the intensity for the SBT/Pt films. The lower part contains the measured spectra and the upper part the calculated ones.

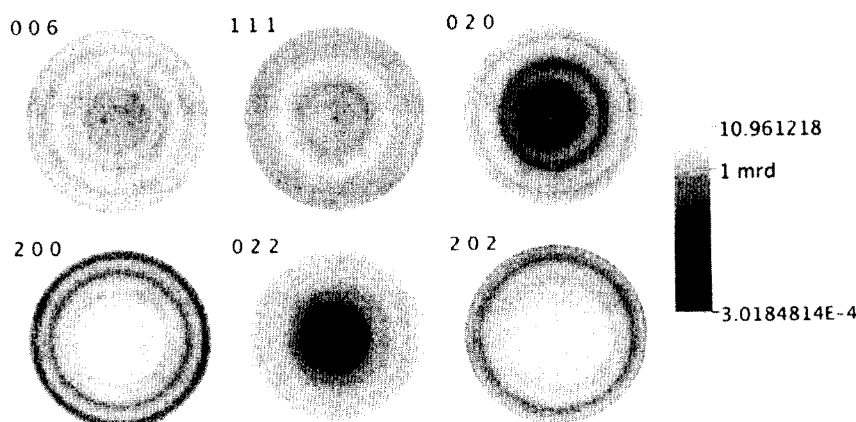

Fig. 5. Recalculated pole figures (log mode) for the SBT layer from the ODF obtained by the analysis.

Again the E-WIMV method was used to model the texture inside the Maud program. A 5° x 5° x 5° cell grid was used in this case and the reconstructed pole figures are visible in figures 5 and 6 for the SBT and the Pt films. Additional information has been obtained from the Rietveld texture analysis approach and in brief: the crystal structure of the SBT has been refined and it is only slightly different from some known SBT structures with different composition; the residual stress state has been analyzed but it was negligible thanks to the spin coating technique and the multilayered buffer

heterostructure used between the SBT film and the substrate. Also the thicknesses of the layers have been refined (though the sensibility of the method in this regard is less than optimal) and confirm the expected ones.

Conclusions

The Rietveld texture analysis approach adapted to the thin film case through the adoption of a layered model has been proved successful in two cases were the traditional approach fails: a case with an extremely sharp texture and another case with a multilayer structure showing completely overlapped peaks. The analysis permits also to obtain other quantities in addition to the ODF, like the strain tensor, the crystal structure (atomic positions and cell) as well as thicknesses of the layers. All corrections are performed at the same time to overcome possible problems. The analysis was possible through the use of a particular X-ray diffraction apparatus constructed ad-hoc for the method to take mutual advantage of both the instrumentation and methodology.

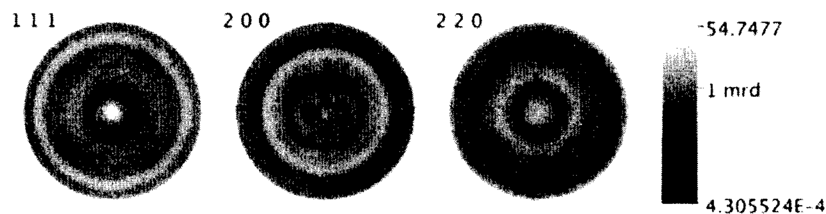

Fig. 6. Recalculated pole figures (log mode) for the Pt layer from the ODF obtained by the analysis.

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