IN SITU THIN FILM CRYSTALLIZATION STUDIES USING HIGH TEMPERATURE GRAZING INCIDENCE X-RAY DIFFRACTION (HTGIXRD)

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Abstract
We describe the experimental procedure and use of high-temperature X-ray diffraction techniques combined with grazing-incidence optics for in situ crystallization studies on several polycrystalline thin films; this technique is referred to as High-Temperature Grazing Incidence X-Ray Diffraction or (HTGIXRD). Temperature calibration techniques, sample positioning issues, and limitations of this analysis technique are discussed. Applications of this technique to crystallization of several ceramic thin films include qualitative investigations such as monitoring phase formation and structural transitions as well as quantitative investigations of crystallization kinetics and crystallite size measurements.

Introduction
Characterization of thin films is of great interest due to the increased use of film structures in modern electronic devices. X-ray diffraction techniques have been employed to study diffusion and stress-strain behavior in multilayered thin-film structures using Bragg-Brantano techniques.[1] With the recent development of grazing-incidence X-ray diffraction, studies such as stress-depth profiling of polycrystalline thin-film structures have been performed.[2] The grazing or pseudo-parallel beam optics allows good resolution of diffraction peaks from a low divergent X-Ray beam at small (< 2°) grazing angles not obtainable by using conventional Bragg-Brentano optics.[3] This allows for better surface characterization of thin films. In this paper we propose extending the use of grazing-incidence X-ray diffraction to high-temperatures for in situ analysis of thin films. We shall refer to this technique as High-Temperature Grazing Incidence X-Ray Diffraction or (HTGIXRD).

The motivation for HTGIXRD analysis stemmed from a desire to obtain in situ high-temperature diffraction information from shallow surfaces. In situ X-Ray diffraction experiments are required to study the crystallization kinetics in thin films. This method can be used to determine the effects of precursor solution chemistry on thin-film kinetics as a function of temperature or to determine the temperature of a structural phase transition. The diffractometer, grazing incidence optics and high-temperature stage are available from most equipment manufacturers, making this technique relatively cost effective.
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Instrumentation

A Scintag X1 diffractometer equipped with a line focus Cu target sealed X-Ray tube, 0.3° incident beam divergence slits, 1° incident Soller slits, 0.4° receiving Soller slits and a Peltier cooled solid state detector was used to collect diffraction data. (More intensity could be obtained with larger active area detectors, however, the sample size tends to limit intensity. If the sample is too large it may not have even temperature distribution.) The high-temperature stage was a Beuhler (Model HDK 1.4) with Pt strip and surround heaters. The maximum operating temperature in air was approximately 1600°C. A type S (Pt / Pt - 10% Rh) 0.01mm diameter thermocouple was used to monitor the strip heater temperature. In order to avoid significant downtime due to potential failures at the welded region on the bottom surface of the heater, it was decided that a small hole be drilled in the center of the Pt strip heater. The thermocouple bead was then placed in the hole and peened into place at the top surface of the strip. This not only made it easier to change thermocouples, if required, but also allowed better control of temperature nearer to the film sample. Calibration would then be required for each thermocouple replaced. In the presence of silicon (or SiO2), platinum based thermocouples may suffer degradation due to reaction of the silicon with the platinum.[4] Therefore caution should be taken in analysis of silicon based thin film samples above 850°C.

Experimental Procedure

SrBi2Ta2O9 "SBT" thin film samples were prepared on Si substrates with platinum electrodes according to a sol-gel spin technique.[5] The Pb(Zr0.3Ti0.7)O3 "PZT 30/70" film was deposited upon a MgO substrate (platinum electrode) using an IMO process described elsewhere.[6] ZrO2 films were prepared on Silicon substrates via a sol-gel technique similar to the SBT films.[7] The thin film wafers were cut to dimensions (10mm x 10mm x 0.5mm) in order to maintain a constant thermal mass. Duplicates of each sample were prepared and initial trial runs were performed on the first few samples to obtain approximate transition temperatures. In this way it was possible to minimize the time for analysis and maximize the obtained information of subsequent runs. Film samples were placed at the center of the strip heater directly above the thermocouple. All diffraction patterns were collected in an air atmosphere.

The Pt heater was first aligned by observing the intensity of the direct beam (40kV/30mA) and then moving the heater stage into the beam until the intensity was reduced by half at the Peltier detector; aluminum strips were placed at the detector to reduce the intensity of the direct beam. Then the stage (omega axis) was rocked back and forth until an intensity maxim was observed. At this point the heater was parallel relative to direct beam. Changing the grazing incidence angle and choosing the divergence slits limits both the X-Ray beam area and height irradiating the sample; this affects both intensity and resolution. The width (or footprint) and height (thickness) of the beam can be easily calculated. See figure 1. Table I shows values for several
divergent-slit / grazing-angle combinations. In order to maximize the intensity, a 2° grazing angle with 0.3 divergent slits was selected for our standard experimental procedures. During the final alignment, a Si substrate with Si 640b powder on its surface was placed on the heater and the goniometer was set to observe the Si (111) peak at -28.4° 2θ. The heater stage was then adjusted to maximize this peak intensity.

Figure 1. A schematic diagram of the pseudo-parallel optics geometry showing the height (H) and width (W) for the X-Ray beam.

Table I: Beam Heights and Widths for combinations of grazing angles and divergence slits

<table>
<thead>
<tr>
<th>Grazing Angle (deg)</th>
<th>Divergence Slit (deg)</th>
<th>Beam Width (mm)</th>
<th>Beam Height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.3</td>
<td>30</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
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<td>10</td>
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</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>60</td>
<td>0.50</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>20</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Temperature calibration was done using melting point standards. These materials were placed on a the surface of a platinized Silicon film and subsequently heated. The observed melting point temperatures were compared to the actual known melting points and a highly linear calibration curve was obtained. Additional calibrations were run biweekly during the course of experimentation with essentially no observable change in the temperature calibration. Figure 2 shows a calibration curve using selected melting point standards. The phase transition of K$_2$SO$_4$
from orthorhombic to hexagonal was observed at 583°C which was in excellent agreement with published results[8] confirming the accuracy of the calibration curve to an error of about 5°C.

Because this was a relatively new experimental setup, there was a desire to know just how reproducible the diffraction data would be. To determine this, Si 640b was placed on a Silicon substrate and the (111) reflection was analyzed in situ on the hot stage. Several diffraction patterns were collected on the (111) reflection at room temperature; the sample was removed and replaced between each run. These (111) peaks were profile-fit to determine the variation of 2θ, integrated intensity, and FWHM. The average Δ2θ of the silicon peak was found to be about 0.02° 2θ and the integrated intensity showed a variation of about 2.5%. An average FWHM value of 0.265(5)° 2θ was obtained for the Si standard; this FWHM value was used as an instrumental broadening value in determining crystallite sizes (discussed later). The peaks tended to show a large asymmetry toward the low 2θ side of the profiles. This observation is a consequence of axial divergence effects which result from the low angle incident beam inherent in the grazing-incidence optics setup.[9] Based on the results of the profile analysis, it seemed likely that the large error in 2θ resulted mostly from a difficulty in reproducing the profile-fit of a given reflection due to its asymmetry and relatively low counting statistics compared to diffraction measurements using the θ-2θ geometry.

Accurate lattice parameter measurement proved to be a very difficult with this experimental setup. There were several sources of error which could result in misleading peak 2θ values. Although true parallel beam optics do not suffer from sample displacement errors, the grazing
incidence geometry can suffer from a slight displacement effect since the beam diverges from the X-Ray source. Hence, the beam does not have a specific grazing angle but rather a range of grazing angles depending upon its divergence from the source (see figure 1). Slight misplacement of the sample within the footprint or height of the beam would change the distribution of grazing-angles that could result in slight shifts in 2θ peak positions. This problem is further complicated by the possibility of hot stage movement as the sample is heated. The convolution of sample motion and beam divergence effects with the sample thermal expansion effects results in a rather difficult assessment of the accurate 2θ position. Therefore, accurate lattice parameter measurements have not been attempted using the current experimental setup.

Results and Discussion
One of the most significant uses of the IITGIXRD technique is the ability to analyze phase formation as a function of temperature. Figure 3 illustrates the formation of a SBT layered-perovskite ferroelectric phase. In this figure we see the initial formation of an amorphous phase in the range of 500-550°C. From 600-700°C there is the formation of an intermediate fluorite phase which then transforms to the layered perovskite ferroelectric phase above 700°C. This information concerning phase formation as a function of temperature (especially information concerning intermediate phases) is extreme valuable for process development of thin films.

Figure 3. Phase formation as function of temperature for the SrBi$_2$Ta$_2$O$_9$ (SBT) layered perovskite ferroelectric.
An additional benefit of the HTGIXRD technique is the ability to analyze phase transformations as a function of temperature. Figure 4 shows the phase transformation of a PZT 30/70 film from the paraelectric cubic phase to the ferroelectric tetragonal phase. The graph displays the (200) peak in the cubic phase splitting into the tetragonal (200) and (002) reflections as the sample is cooled. Due to the large FWHM (and hence lower resolution) it was difficult to establish exactly where the peaks split as the phase transforms. It was possible to look at the change in the FWHM in the different profiles, though, as an indication when the cubic (200) profile began to split into two reflections. The profile fitting of the diffraction peaks between 550°C and 450°C indicated that the phase began to transform between 470 and 450°C. This was noted by the significant broadening of the 470°C and 450°C profiles compared to those at higher temperatures. This data was consistent with dielectric constant measurements collected on this sample which indicated a phase transformation near 475°C.

We also investigated cubic ZrO₂ phase formation for films prepared using a sol-gel type procedure. The HTGIXRD technique shows some promise here for quantifying phase formation data for thin films. Figure 5 illustrates the monitoring of a cubic zirconia (111) reflection as it grows out of the amorphous phase. As demonstrated in figure 5, the sample was heated directly to 370°C and then held while diffraction patterns were collected from 27°- 33° 2θ. Each scan required about 6 minutes of data collection time with about a minute delay between each scan. The peak profiles were fit to determine peak areas which were then plotted as a function of time as shown. There appears to be an initial incubation period of about 1 1/2 hours where the amorphous phase is present. This is followed by a region of crystallization were the peak area changes rapidly over about 45 minutes. As the peak area reaches a plateau there is a
region of stabilization where there is significant integrated peak intensity variation. This intensity variation begins to level out after about one hour and after four hours of holding at 370°C the peak area appears to have become constant. This data is useful for optimizing processes involving phase formation of thin films and also furnishes interesting information about how the sample is behaving before, during, and after crystallization.

![Graph](image)

**Figure 5.** Phase formation of cubic ZrO$_2$ from a Sol-Gel deposited solution. The film sample was held at 370°C for ~5 hours. Diffraction scans were collected approximately every 6 minutes.

Crystallite size determination was also investigated using HTGIXRD. This analysis was performed on a film which was correspondingly analyzed using Scanning Electron Microscopy (SEM) to compare the observed crystallites to that of the XRD results. As discussed earlier, Si 640b was used to determine the instrumental broadening for our experimental setup which we determined to be ~0.26° 20 FWHM. A sample film of a Sr-Bi-Ta-oxide pyrochlore phase[10] was chosen as a prototype sample since the crystallite size was large enough to measure with SEM, but small enough to significantly enlarge peak profiles. Diffraction peaks were collected on the pyrochlore film using the grazing incidence setup. Then the profiles were fit to determine the FWHM values for the pyrochlore peaks. Crystallite size values were determined using the Scherrer equation[11] (assuming all broadening was due to crystallite size). Our GIXRD analysis of the pyrochlore film predicted a crystallite size of 180(40)Å. This was compared to the SEM analysis where measured grain sizes appeared to be in the range of 270(80)Å. The XRD values were slightly lower than those observed by SEM but they are still within the error.
of the analysis. A likely explanation for the slightly low value of crystallite size predicted by the XRD analysis resides in the assumption that all peak broadening is due to crystallite size effects. Since the sample is a film structure it is likely that there is also some microstrain present in the sample that also contributes to peak broadening. Another possible reason for the grain size discrepancy in the film is that the coherent domain size is smaller than the observed grain size as viewed by SEM.

Summary
HTGIXRD has proven very useful in qualitative X-Ray analysis of thin films. Specifically, this technique is quite useful for phase identification, phase formation as a function of time/temperature, and also for crystallite size determination. Additionally, HTGIXRD shows some promise for use in quantifying reaction kinetics for thin films. This technique has important implications for future investigations since it opens the door to real-time process development of thin film materials.

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References