

Example of Non-Conventional Grazing angle diffraction on Scintag X2:

(Data provided courtesy of Mustafa Telli, PhD graduate student of Susan Trolier-McKinstry)

Grazing angle diffraction is a technique employed whenever there is a need to see only the surface of a sample, such as in the analysis of thin films. In our laboratory, our Scintag X2 (Scintag 3) is capable of being switched into this type of goniometer geometry with relative ease.

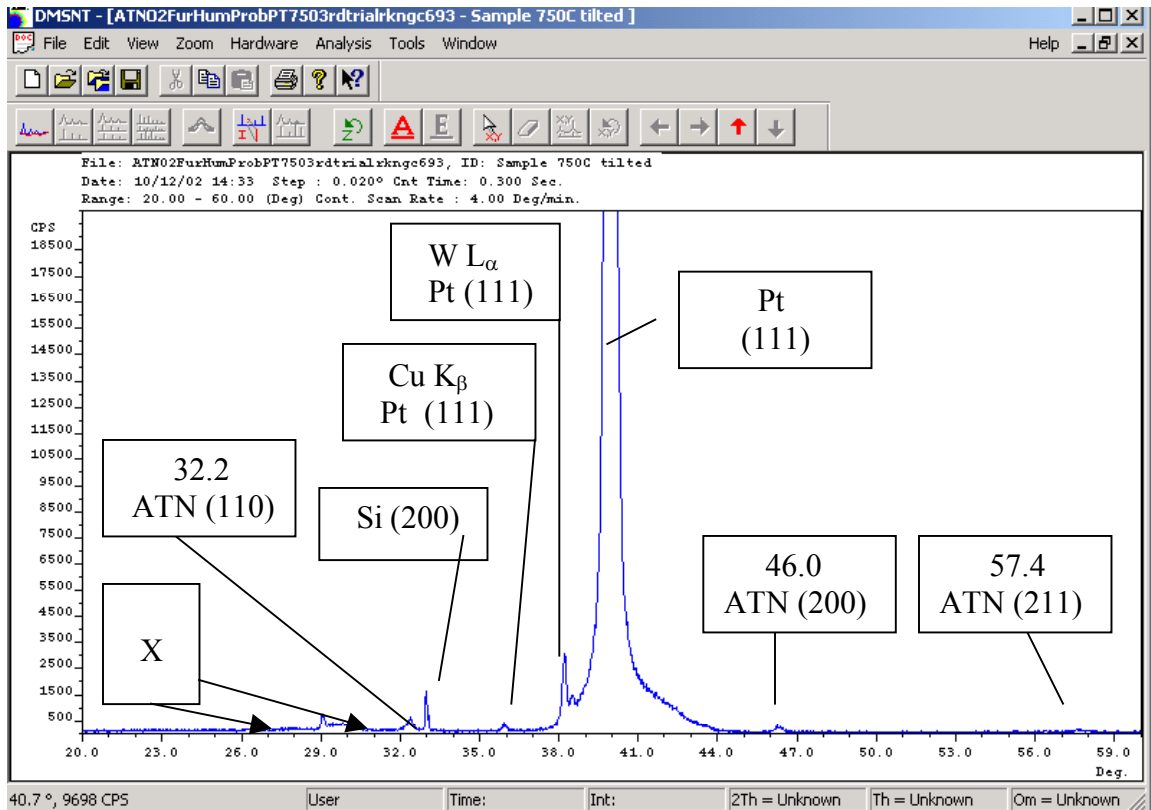
In normal, Bragg-Brentano powder diffraction, two axes move in sequence with each other. In our Pad V units (Scintag 1 and 2), the sample and the detector move together in a gear ratio of 1:2. In other words, the detector moves twice as fast as the sample or the sample position is half that of the detector. This type of geometry is known as theta-2-theta geometry. When the X2 is operating in normal powder diffraction mode, there are also two axes moving in sequence with each other, but in this case the x-ray tube and the detector move together at the same speed and at the same angle. This is known as theta-theta goniometer geometry.

When one looks at a thin film in normal powder diffraction in either of these mentioned geometries, there is generally a very large peak contributed by the sample substrate (often silicon). The intensity of this peak is often so high that it swamps out the peaks of the film or it may directly overlap the film peaks of interest. Figure 1 is a pattern collected in normal powder mode from a silver tantalum niobate (ATN) film sample with the following cross section:

(Note: There is thought to be a reaction layer either between the ATN film and the platinum layer or between the titanium and SiO₂ layer.)

Silver Tantalum Niobate (ATN) film (~450 nm)
(Possible reaction layer location)
Pt (~150 nm)
Ti (~20 nm)
(Possible reaction layer location)
SiO ₂ layer (~1000 nm)
Silicon [(100) orientation] substrate

Figure 1

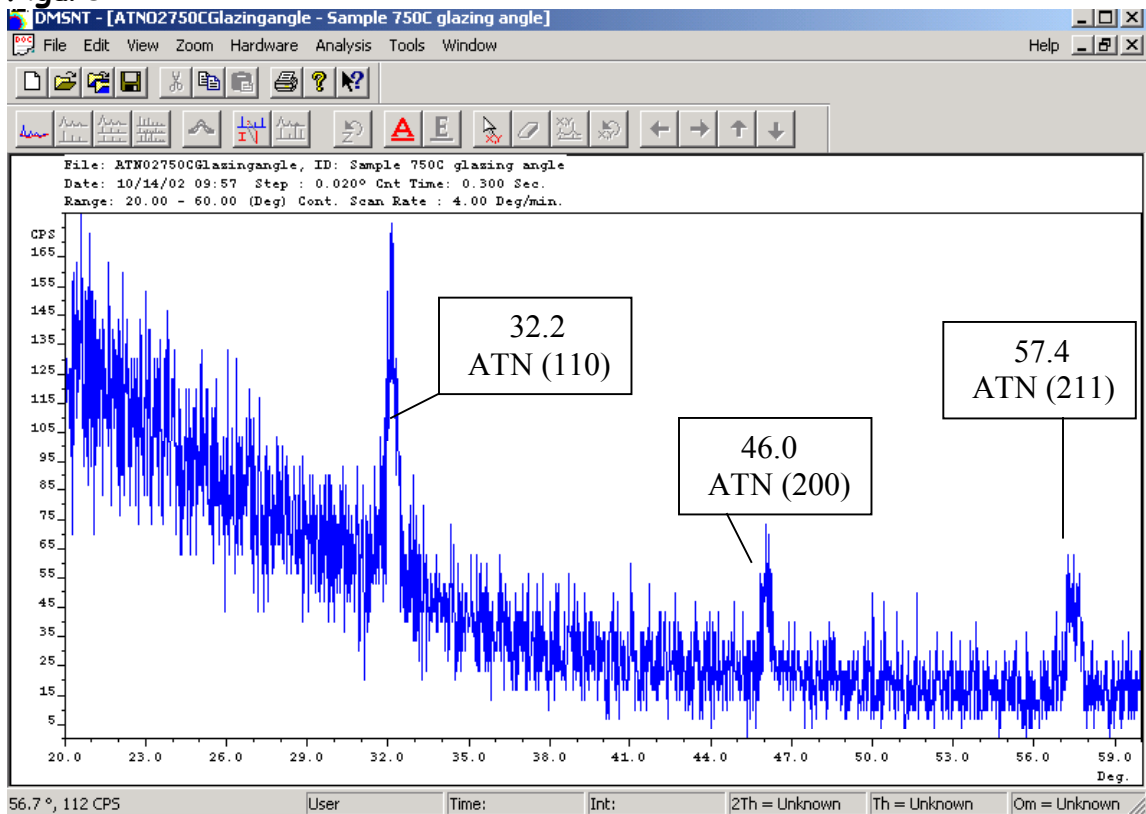


The peaks noted at 32.2, 46.0 and 57.4 degrees 2-theta correspond to the silver tantalum niobate (ATN) film. The large peak in the center of the pattern belongs to the platinum layer. Other peaks are labeled accordingly.

Figure 2 shows the diffraction pattern collected for the same sample in thin film, or grazing angle geometry. Note that the only peaks visible are those corresponding to the film.

In this case, we are using theta-theta geometry, but instead of moving both the x-ray tube and the detector, the x-ray tube is fixed at a low angle while the detector scans across the 2-theta area of interest. Because the source is positioned at a very low angle relative to the surface of the sample, (2 degrees), the x-rays "graze" the surface rather than penetrate into the sample. Thus, only the film diffracts, and not the substrate underneath.

Figure 2



In the above figures, the peaks from the film are clear from the platinum peak (non-overlapping) and can be distinguished in normal powder diffraction mode. Many times, the platinum peak directly overlaps the peaks of interest, making grazing angle geometry the only option to see peaks belonging to the film. Since that is not the case here, a logical question is, "Why use grazing angle geometry for this sample?"

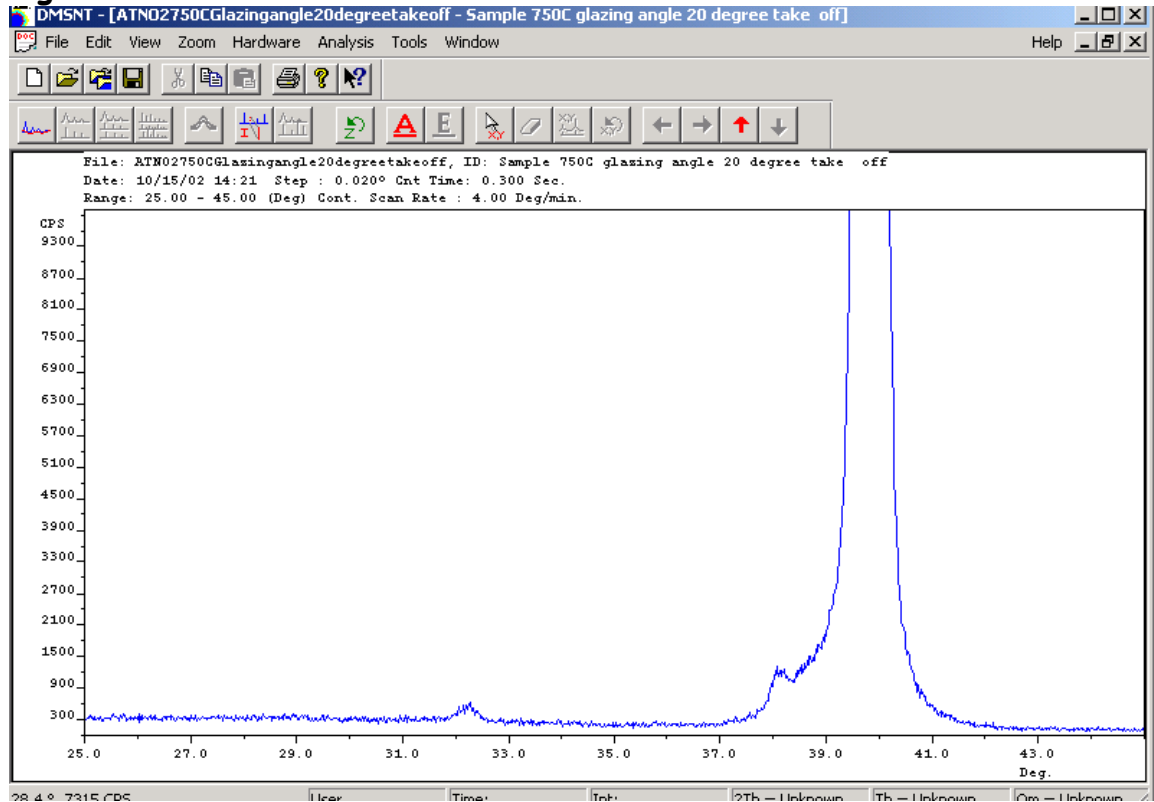
The goal of using grazing angle geometry here is to investigate the area marked "X" in Figure 1 above. Area "X" consists of a sharp peak at 29.0 degrees 2-theta and a wide band between 29.0 and 30.5 degrees 2-theta. The wide band of peaks is thought to correspond to the silica layer. The sharp peak at 29.0 degrees is thought to correspond to an unknown reaction layer. It is thought to be located either between the titanium and the SiO_2 layer, or between the ATN film and the Pt layer. We have attempted to determine a range of grazing angles where we see first the film, then the film and the reaction layer (if it exists and if this is its true location), then the film, the reaction layer and the platinum layer appear. If it can be

shown that these layers appear with increasing grazing angle, this will support the theory of the existence of this reaction layer in this position.

Use of the grazing angle technique in this fashion is rather non-conventional in that to be considered "grazing," a very low angle is used for the tube setting. In this case, a minimum of a 20-degree grazing angle is required before the platinum substrate becomes visible. Maximum grazing angle for conventional thin film experiments is about 7 degrees.

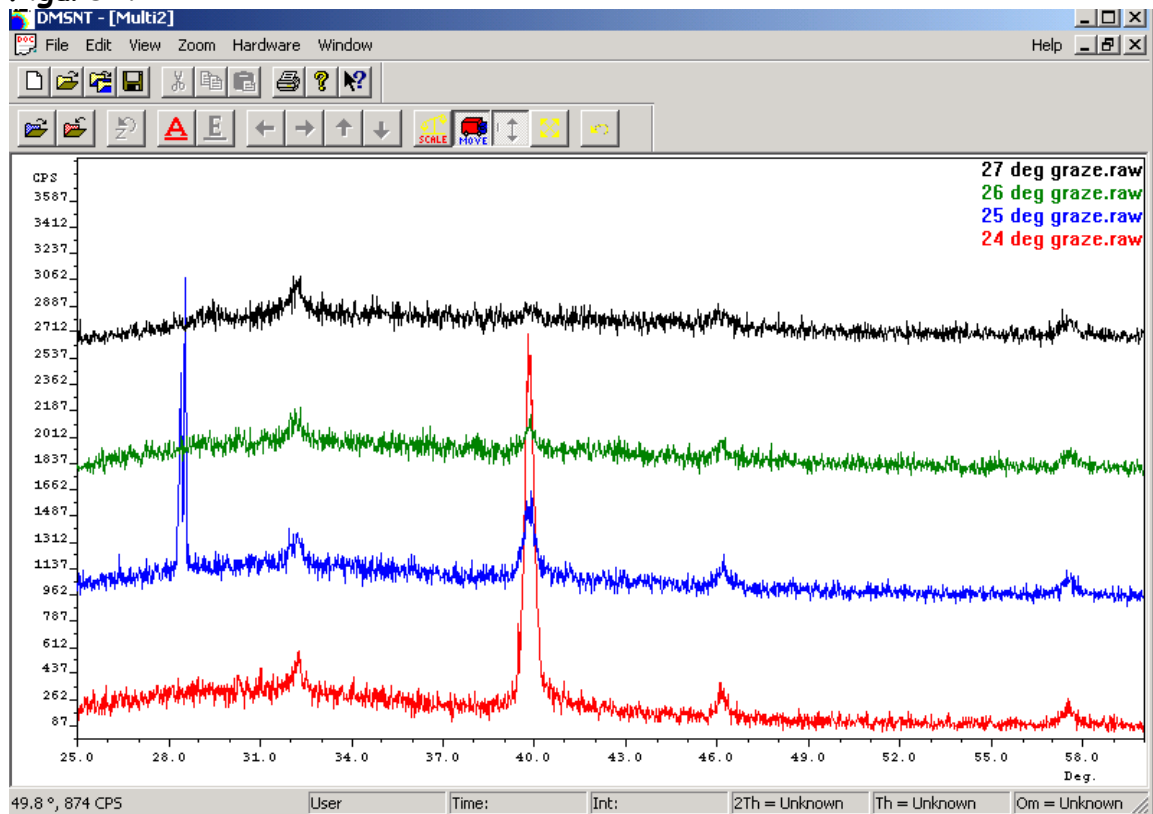
Figure 3 shows the diffraction pattern obtained at a 20 degree grazing angle. Note that the film peak at 32.2 degrees is present as is the platinum peak.

Figure 3



As the grazing angle is increased, (Figure 4), shown here, increasing from 24 to 27 degrees, the platinum peak fades, but the film peaks are still apparent. There is also an additional peak at approximately 28.5 degrees 2-theta for the 25 degree grazing angle scan.

Figure 4



This peak at 28.5 degrees 2-theta in the 25 degree grazing angle scan is too low (28.5 versus 29-30.5 degrees 2-theta) to correspond to the hypothesized reaction layer at 29.0 degrees 2-theta in Figure 1. Further investigations are needed to determine the source of this unknown peak.

So, the grazing angle technique is not able to confirm the presence of the silica reaction layer in this example. It hints that the reaction layer is probably not between the ATN film layer and the Pt layer, because we would expect to see a corresponding peak in the 20 degree grazing scan (or before) where the Pt peak first becomes visible. The value of this example is to provide a good comparison of the type of data obtained with normal powder data as compared to that obtained with grazing angle diffraction, and to present a non-conventional use of traditional grazing angle methodology that may prove successful for other layered thin-film samples.