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Abstract

In this paper, we report the results of a follow-up study of the d vs. $sin^2\psi$ plots from W thin films. It is shown that the oscillatory behaviour can be the result of the phase transformation from the metastable β-W, which can cause the formation of two layers with opposite stresses in single-phase α-W films.

1 Introduction

The classical methods for x-ray stress-strain analysis enjoy widespread use. The basic theory underlying these techniques is based on continuum elasticity analysis and has been well known for over 60 years. An excellent review article[1] published in 1966 covers most of the basic theory in use today. In its most basic form the theory applies rigorously to isotropic, homogeneous materials that diffract in the kinematical limit. Since this ideal is rarely achieved, numerous additions, extensions, and clarifications to the basic theory have been proposed over the past three decades. Due to the limited applicability of most of these extensions, their practical benefits have not been in proportion to their number. Improper application of the basic theory or its extensions can cause errors in both the sign and the magnitude of the calculated stress fields and may lead to wrong conclusions.

In the literature there is general agreement that the complex strain fields that can form in polycrystalline materials are the main cause of the deviations from theoretical predictions. These deviations can be observed even in "model" materials like tungsten which, given textbook data, should be closest to the theoretically ideal state. In this article we discuss the strain fields in thin films of tungsten deposited by dc-magnetron sputtering and their effect on d vs. $sin^2\psi$ plots that are used in x-ray stress analysis.

2 Literature Review

In standard mechanical metallurgy textbooks[2] W is reported as being the only metal with isotropic elastic constants. While this is certainly the case for large specimens, it is well known that the properties of thin tungsten films depend very strongly on the way the film is prepared: In dc magnetron sputtering tungsten films can deposit as single-phase α-W with the (equilibrium) BCC structure, as metastable β-W with the A15 (cubic) structure or as a mixture of the two, depending on the partial pressure of oxygen in the chamber, the film thickness, substrate bias, temperature and deposition power[3, 4]. It is generally agreed that after a critical thickness, t_c, is reached (typically 50 nm for the power levels used), the β-W crystallites in the sputtered film transform to α-W and the grains deposited during further sputtering form in the equilibrium BCC structure. The phase transformation is generally considered to be thermally induced [3, 5], even though transformations at room temperature over long periods of time have also been reported[5, 4]. In certain cases this transformation yields two layers of α-W with opposite stresses[5, 6]. The presence of these two layers can cause asymmetry in the diffraction peaks of the α-W, with the presence of the layer under tension manifesting as a shoulder on the high 2θ side. In the first report of this problem[5] where film thicknesses between 25 and 200 nm were studied, the tensile layer was around 25 nm thick for the entire deposition range. Consequently, due to attenuation by absorption, the asymmetry became insignificant for film thicknesses over 200 nm. However, the asymmetry could be reproduced by etching the film back, indicating that the thin layer under tension still existed adjacent to the substrate. Since the presence of this second layer caused serious complications in stress analysis, results were reported only from the 25 nm film and the 200 nm film (by which thickness it was assumed that the effects of the initial layer were negligible). Both films exhibited linear d_{hkl} vs. $sin^2\psi$ plots and, thus, could be treated with the standard x-ray stress analysis.

In contrast, in a paper presented at the 1995 Denver X-ray Conference, we reported the measurement of oscillatory d vs. $sin^2\psi$ plots from W thin films[7]. Since these films were much thicker (nominally 1000 nm) and did not show any peak asymmetry (despite being rather broad), transformation stresses were not considered to be a factor among the causes of oscillations. Furthermore, since the anisotropy index of BCC α-W is very close to unity[2], the elastic constants along all lattice directions are equal and the overall polycrystalline aggregate can be considered isotropic in elastic loading. Consequently, these oscillations could not be attributed to the effects of elastic anisotropy. Two other possible causes; inhomogeneous plastic flow and micro-cracking were considered since the breadth of the x-ray peaks at half-maximum intensity, which is sensitive to plastic flow, varied with $sin^2\psi$. In addition, some films exhibited spallation and cracking with the typical "worm" cracks [8]. The stress profiles around the cracks are functions of the distance from the crack and, thus, could cause the heterogeneous strain distribution necessary for the oscillatory d vs. $sin^2\psi$ plots.

These explanations, on the other hand, were incompatible with the sample and deposition symmetry arguments, and, thus, were less than satisfactory. In a recent paper[6] we reported untransformed β-W layers over 100 nm thick and showed that asymmetric peak profiles could be observed from 400 and 600 nm thick single-phase α-W films. This information raises the possibility that the oscillations in d_{hkl} vs. $sin^2\psi$ plots of magnetron sputtered W films can be caused by the transformation from β to α W. In this paper, this hypothesis is tested.

3 Experimental Details

50, 100, 400 and 600 nm thick W films were deposited on glass and Si substrates (both 100 and 111 type) through dc magnetron sputtering. Prior to deposition, the system was pumped overnight to a base pressure of $2x10^{-7}$ Torr. The deposition took place at 500 W, with Ar gas pressure at 10^{-3} Torr after a pre-sputter of 30 minutes. The deposition rate was nominally 30 nm/min. The substrates were at room temperature at the beginning of the deposition.

For phase identification and stress analysis a horizontal Rigaku powder diffractometer with a rotating anode power supply and a graphite diffracted beam monochromator was used with Cu radiation. The goniometer radius for these measurements was approximately 185 mm. For phase identification, the system was used in the thin film mode, with a .2 degree divergent slit, 5 degree scatter slits on both divergent and receiving arms and a vertical soller collimator in the "parallell beam" mode on the receiving arm. For the stress analysis, focussing geometry with a 1 degree, 1 degree scatter slits and .3 degree receiving slits were employed. The 321 α W reflection around 129 degrees 2θ was used for stress analysis. Peak asymmetries were also characterized at the X20C beamline of NSLS, Brookhaven National Laboratory. A vertical Huber diffractometer, operated in the two circle mode was used in these scans. Monochromatic radiation with a wavelength close to Cu K-$\alpha - 1$ was employed. The absence of the K-$\alpha - 2$ component in this set of experiments proved to be important in the interpretation of the data obtained from the laboratory instrument.

4 Results and Discussion

The laboratory powder (thin-film) scans from the W layers are shown in Figure 1. In Table I, the reflections and their approximate diffraction angles for α-W and β-W phases are shown. Comparing this table with Figure 1, it can be seen that both the 50 nm and the 100 nm thick films are two-phase mixtures of the α and β phases. Nominally, the fraction of β phase in the 100 nm thick film is smaller, based on the relative intensity of the 112 reflection at 43 degrees 2θ. The 400 and 600 nm films are nominally single phase α tungsten. However, there is still a finite but very small β 002 peak visible around 35 degrees 2θ even for these films.

Precision scans of the individual peaks show asymmetries in the peak profiles for most of these films. There are two types of asymmetries. In the case of the two phase films, most low index α reflections also have β peaks in close proximity (Table I).

Reflection	Phase	Approximate 2θ
002	β	35.28
012	β	39.61
110	α	40.27
112	β	43.58
200	α	58.26
222	β	63.33
023	β	66.24
123	β	69.08
211	α	73.19
004	β	74.63
024	β	85.33
220	α	87.01
124	β	87.97
233	β	90.6
310	α	100.65
025	β	109.39

Table 1: The reflections and their approximate diffraction angles for α-W and β-W phases. The data is calculated for Cu K_α radiation with lattice constants of 3.1648 and 5.047 angstroms respectively for the two phases[10].

Consequently, some overlap and peak asymmetry is expected in these peaks.

The second kind of asymmetry occurs in the peak profiles for the single-phase α-W films for all reflections (Figure 2). In this experiment, this asymmetry was most pronounced in the 400 nm thick film, with the α-W reflections from the 100 and 600 nm thick films exhibiting significantly less asymmetry. This second type of asymmetry occurs from the summation of the diffraction peaks from two distinct α-phase volumes as discussed by Vink et. al[5]. The first peak originates from W grains that deposited as BCC-α from the sputtering plasma. These primary α-W grains are under very strong compressive stresses in the plane of the film. This film stress, generally attributed to atomic peening, causes Poisson expansion of the atomic plane spacings along the film surface normal. Consequently, for the primary α-W, the peaks for all reflections move to 2θ angles lower than those for an unstressed film.

The second peak contributing to the asymmetric single-phase α-W reflections originates from BCC-α grains that formed through the transformation of the A15-β phase. The stress state in these secondary α-W grains will depend on their location. The cubical dilatation associated with the transformation from the A15 to the BCC structure is approximately -0.94%[5]. The shrinkage in the transformed grains will be constrained by the surrounding (primary) α grains and, at the boundary, by the substrate. If the transformation were to occur in a β grain completely surrounded by primary α grains, the transformed grain would be placed in hydrostatic tension[9]. In this case, the strain along the normal to the film surface would also be tensile, and the peak would shift to lower 2θ (larger plane spacing) values. If, on the other hand, the transformation is constrained primarily by the substrate and the transformed grains are free to expand and contract along the film normal, an isotropic tensile stress would form in the plane of the film. Consequently, the strain along the surface normal would be compressive due to the Poisson contraction and the peak of a symmetric reflection would shift to higher 2θ (smaller plane spacing). Since the observed peak asymmetry is on the high 2θ side for all cases, the second hypothesis seems to be the correct one. Thus, even for these thicker films, most of the β phase exists as a layer and not as discrete grains embedded in the matrix. To test the hypothesis further, the 400 nm film was removed from its substrate. The film fragments curled upon removal indicating the presence of a stress gradient with depth. If the strain distribution were homogeneous, the film would have remained flat. The asymmetry of the α-W reflections also disappeared after the removal(Figure 3-b,c). This indicates that the (opposite) stress states in both the primary and secondary α-W layers are balanced, in large part, by stresses in the substrate.

Stress analysis from the films with asymmetric peak profiles is not a trivial task. First of all the two peaks that combine to form the observed asymmetric peak must be deconvoluted and analyzed separately. This requires some care. As can be seen from Figure 3-A, the 321 reflection obtained from the laboratory system can be easily mistaken as the Cu $K_{\alpha-1}$-$K_{\alpha-2}$ doublet. In Figure 4-A, the d vs. $\sin^2\psi$ plot obtained under this assumption is shown. The plot is nominally linear, contains no ψ-splitting and can be analyzed to yield a stress of -2.72 GPa using theoretical x-ray elastic constants[11]. The error, if only calculated from the standard deviation of the regression fit is $\mp$78 MPa ($\mp$ one standard deviation).

Given the findings previously reported in the literature, this result seems very reasonable. In fact, if one only considers routine laboratory data for the 400 nm film, a self-consistent picture emerges:

1. The fast theta-2theta scans shown in Figure 1 show a single-phase film for the

400 nm film.

2. The 321 peak profile shown in Figure 3-A for this film appears to have a rather broad $K_{\alpha-1}$-$K_{\alpha-2}$ doublet.

3. The d vs. $\sin^2\psi$ plot obtained from the deconvolution of the 321 peaks under this assuption is quasi-linear (figure 4-A).

All of these findings imply a single-phase film with a homogeneous stress profile. Unfortunately, this is erroneous: The synchrotron data shown in Figure 2 indicates that the asymmetry exists for all reflections for this film including the 321. Since monochromatized synchrotron radiation contains no emission lines and, thus, no Cu $K_{\alpha-1}$-$K_{\alpha-2}$ doublet, the peak-analysis leading to Figure 4-A (assuming an asymmetric peak due to the doublet) is not satisfactory. Consequently, the laboratory profiles were fitted with two Cauchy peaks, each possessing the Cu $K_{\alpha-1}$-$K_{\alpha-2}$ doublet. This enabled the determination of two plane spacings at each ψ corresponding to the primary and secondary α-W domains. The two d vs. $\sin^2\psi$ plots obtained by this analysis from the 321 reflection of the 400 nm film are shown in Figures 4-b,c and correspond, respectively, to the primary and secondary α-W domains.

The d vs. $\sin^2\psi$ plot from the primary α-W layer is nominally linear (Figure 4-B), indicating the presence of a quasi-homogeneous strain state within this domain. Analysis of figure 4-B with a linear least-squares fit yields -2 GPa for the in-plane stress of the primary α regions.

The secondary α-W grains yield non-linear d vs. $\sin^2\psi$ data (Figure 4-C), with the tilts at the low ψ angles showing a tensile trend, which is reversed after ψ=36 degrees. These data may be analyzed to yield a stress gradient with depth in the W-film. The data available at this time, however, are not sufficient to do do this analysis. It must be noted that the presence of asymmetry from both Cu $K_{\alpha-1}$-$K_{\alpha-2}$ doublet and the heterogeneous strain distribution necessitates higher resolution data than is available with a graphite difracted beam-monochromator; The raw data obtained from the 400 nm film after its removal from the substrate can be fitted with a single Gaussian peak (3-C) or double Lorentzian peaks (3-B) with equivalent residuals. Consequently, the peak position(s) determined with multiple peak fits may not be unique. A detailed characterization of the peak profiles as a function of glancing angle is in progress for this purpose and will be reported later. Finally, it is interesting to note that, despite large non-linearity in the data from the secondary α-W domain, negligible ψ-splitting is observed for both domains. This indicates the absence of shear strains along the surface normal as expected from equilibrium and symmetry considerations.

In summary, even though BCC-W has isotropic elastic properties, magnetron sputtered thin films may have heterogeneous residual stress states due to the phase transformation from the metastable β-W to the BCC α-W structure. Overall, this transformation can yield a two-layer structure with opposite stress states. It seems that these effects can persist in films much thicker than the critical thickness values reported in the literature. The heterogeneous distribution of the transformation strains in such films can be partially responsible for the oscillatory d vs. $\sin^2\psi$ behaviour previously reported. It must be noted that if microstress measurements are carried out on such films where only a few grains are sampled, the type and location of grains may introduce large variations in the stress state despite their isotropic elastic constants, resulting in strongly oscillatory d vs. $\sin^2\psi$ data. Such data should not be analyzed using the linear approximation commonly employed in practice. Furthermore, the absence of such effects must be experimentally verified on a case-by-case basis, checking all available reflections and multiple ψ tilts, given the large variability in W microstructures reported in the literature.

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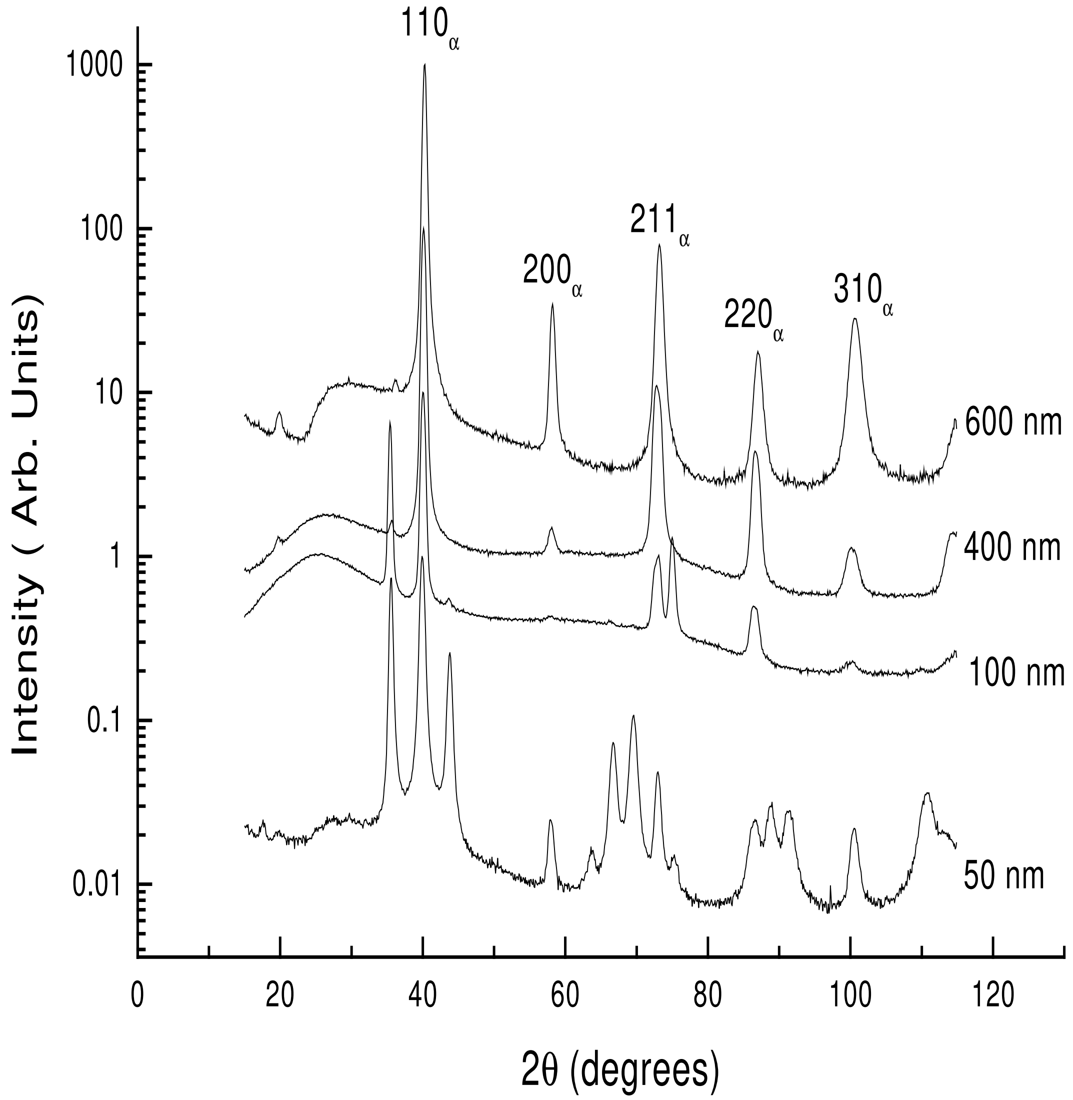

Figure 1: Theta-2Theta scans of the W films of different thicknesses. The normalized intensities have been offset by an order of magnitude for each film for clarity. The location of the BCC α-W reflections are also shown.

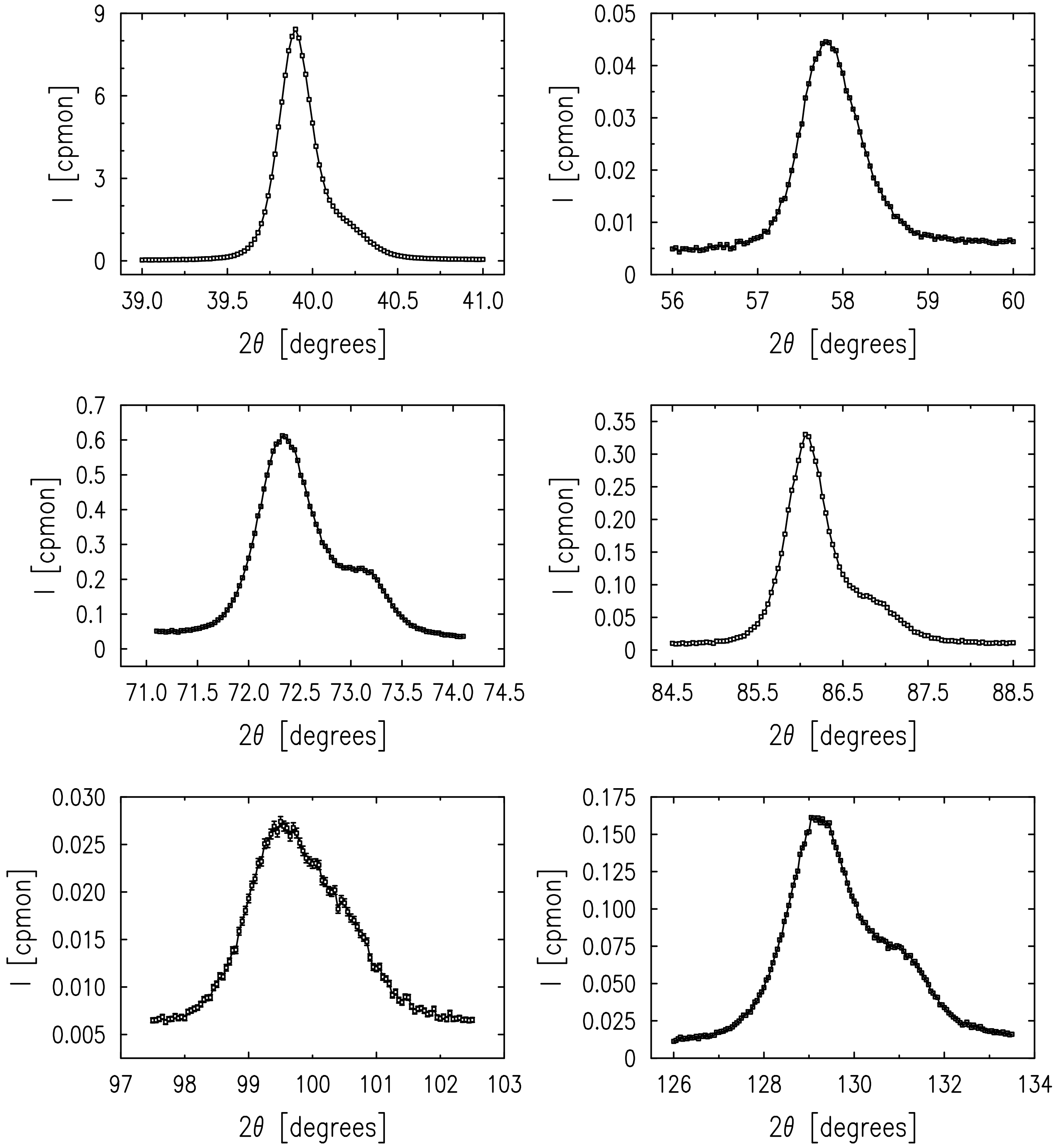

Figure 2: Precision theta-2theta scans of the 400 nm W film for the 110, 200, 211, 220, 310 and 321 α-W reflections. Monochromatized synchrotron radiation at NSLS X20A beamline was used for these scans. The asymmetry of the peaks are caused by diffraction from two α-W domains with different strain states.

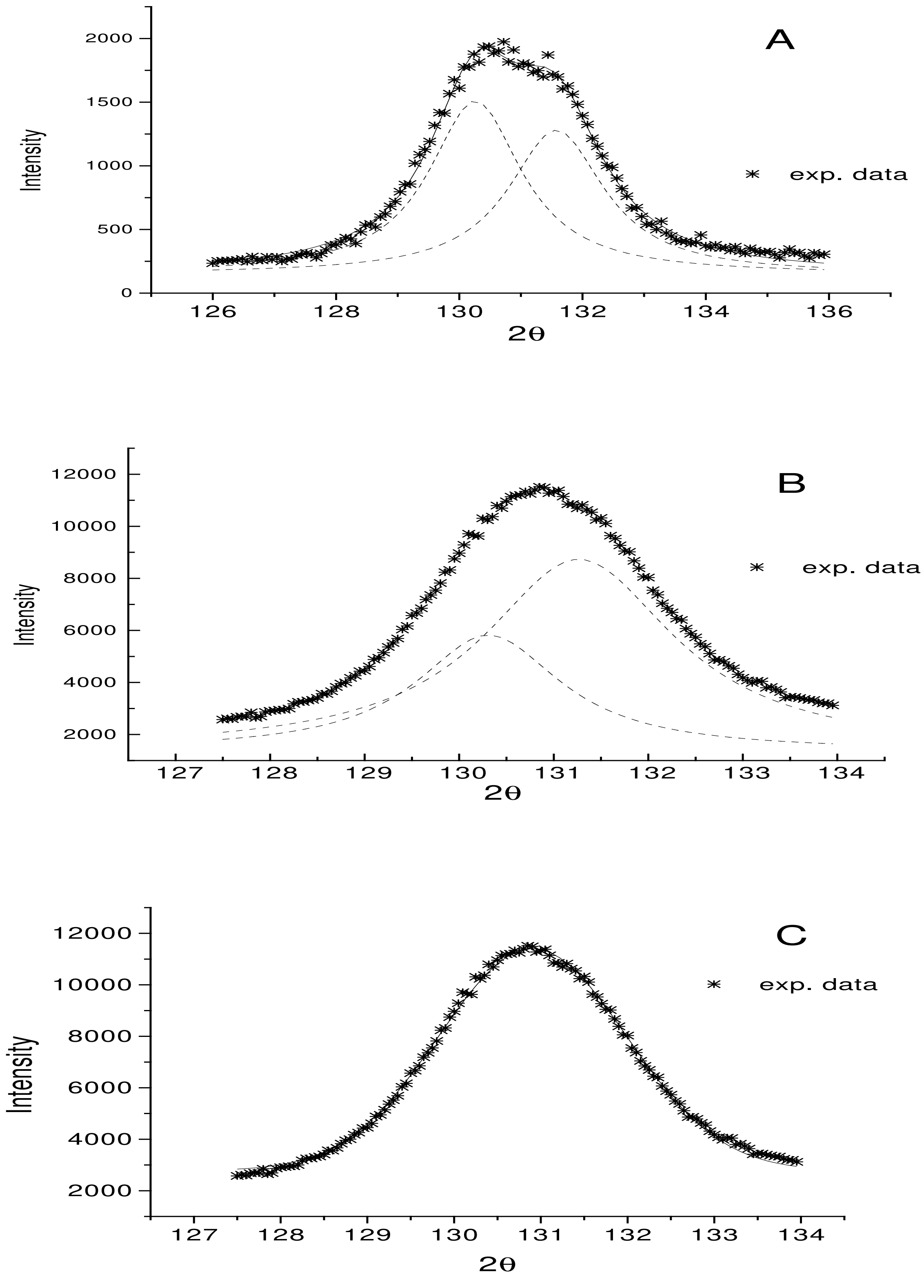

Figure 3: The 321 reflection of the 400 nm thick film at ψ=0 on the substrate (3-A) and off the substrate (3-b). In each case the fitted functions are also shown (dashed lines). The data from the free film can also be fitted with a single Gaussian (3-C).

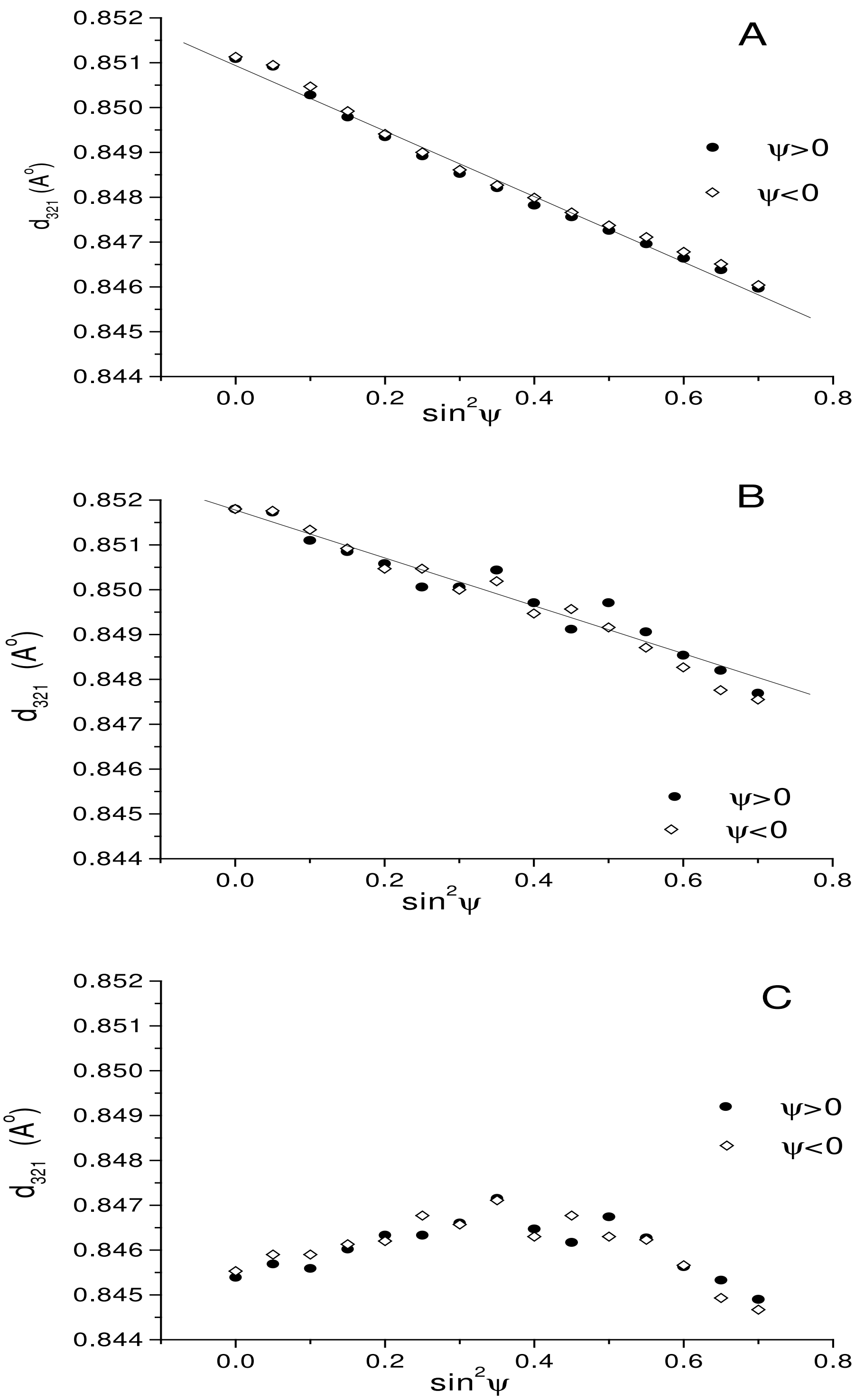

Figure 4: $d_{\psi} vs. sin^2\psi$ plots for the 321 reflection of the 400 nm W film obtained under different assumptions. Figure 4-A neglects the presence of primary and secondary α-W. Figures 4-B and C are calculated from the deconvolution of the 321 peaks into contributions from the primary and secondary α-W domains and reflect the strain states in these domains respectively.