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J. Phys.: Condens. Matter **16** (2004) 1751–1760 PII: S0953-8984(04)73199-9

Stress relief and texture formation in aluminium nitride by plasma immersion ion implantation

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Received 8 December 2003, in final form 2 January 2004
Published 27 February 2004
Online at stacks.iop.org/JPhysCM/16/1751 (DOI: 10.1088/0953-8984/16/10/007)

Abstract

The effect on the intrinsic stress in AlN films of applying pulsed bias during cathodic arc deposition has been studied. We find that the stress depends only on the pulse voltage–pulse frequency product, Vf. The form of the dependence is well fitted by an exponential function whose parameters can be interpreted physically. The preferred orientation changes progressively with Vf, from hexagonal crystallites having their $\langle 0001 \rangle$ direction in the plane of the film at low Vf, to hexagonal crystallites having their $\langle 0001 \rangle$ direction normal to the plane of the film at high Vf. The $\langle 0001 \rangle$ in-plane orientation may be consistent with energy minimization in a biaxial stress field whereas the $\langle 0001 \rangle$ normal orientation is consistent with the alignment of a channelling direction with the ion beam.

1. Introduction

Aluminium nitride (AlN) has many useful properties as a thin film, including high electrical resistance, high thermal conductivity, large direct bandgap and low thermal expansion coefficient. It is very hard, wear resistant and chemically stable, making it attractive as a coating for biomaterials applications. It is also transparent in the visible and infrared regions.

The level of intrinsic compressive stress induced by energetic ion impacts during film growth is a key property in determining the likelihood of subsequent delamination of the film. Structural properties of the film, including preferred orientation or texture, may also be correlated with stress. In a previous work [1] we studied the effect of DC bias in the range 0–350 V on the intrinsic stress and properties of AlN films. By applying DC bias of 350 V to a film of AlN during deposition from a cathodic arc operating in nitrogen gas, we have

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Table 1. Parameters used for deposition of AlN films on Si(100) substrate.

Deposition conditions	Set values
N_2 flow rate	5.0 sccm
Ar flow rate	3.7 sccm
Arc current	60 A
Residual base pressure	10^{-5} Torr (1.3×10^{-3} Pa)
Deposition pressure	1.9×10^{-3} Torr (2.5×10^{-1} Pa)
Substrate bias voltage	2–9 kV
Frequency	50–1000 Hz
Deposition time	5 min

shown that we can reduce the intrinsic stress in AlN films to below 1.2 GPa [1]. The stress reaches a maximum at a DC bias of 200 V and decreases with further increase in ion bias to 350 V [1]. The film with highest intrinsic stress (4 GPa), deposited with a DC bias of 200 V, had an electron diffraction pattern consistent with AlN crystallites with the hexagonal zincite structure oriented with their c axes lying in the plane of the film [1].

The application of pulses with voltages in the range 1–20 kV to an object immersed in a plasma to cause ion bombardment is known as plasma immersion ion implantation (PIII). In this paper, we extend the previous work [1] to study the dependence of stress and preferred orientation of the AlN films on the PIII parameters of pulse voltage ($\boldsymbol{V}$) and pulse frequency ($\boldsymbol{f}$). To assess the form of the dependence of stress on the PIII parameters, we fit the data for stress as a function of the Vf product using two models, the exponential model and the percolation model. We also correlate the stress with the preferred orientation with the aim of investigating the mechanisms that cause preferred orientation.

2. Experimental details

The AlN thin films discussed in this paper were fabricated using a filtered cathodic arc deposition system which has been described elsewhere [2]. The cathode used was a 50 mm diameter aluminium disc of purity 99%. The arc current was 60 A and curved magnetic field coils were used to steer the plasma to the substrate and eliminate macroparticles for the deposition of all films. Silicon wafers of average thickness 320 μm polished on both sides were used as substrates. High voltage pulses were applied to the substrate during growth using a PIII (PI^{3TM}) high voltage pulsed power supply from ANSTO. The pulse bias and frequency were varied while the pulse length was held constant at 20 μs. The film thickness was measured using a Tencor P10 surface profiler.

Prior to deposition, the substrates were cleaned in an Ar plasma discharge created using the PIII power supply. In this process, negative bias pulses (3 kV, 1200 Hz) were applied to the substrate holder for 7.5 min. The base pressure prior to deposition was approximately 10^{-5} Torr (1.3×10^{-3} Pa). A summary of the deposition conditions is given in table 1.

The intrinsic stress in the samples was determined by measuring the change in the radius of curvature of the Si substrate before and after deposition. This change was measured in two orthogonal directions using a surface profiler. The intrinsic stress σ_f is given by Stoney's equation [3]:

$$\sigma_f = \frac{E_s}{6(1-\nu_s)}\frac{t_s^2}{t_f}\left(\frac{1}{R} - \frac{1}{R_b}\right)$$

where E_s is the Young's modulus for the Si(100) wafer (125 GPa), ν_s is the Poisson's ratio for the Si substrate (0.28), t_s is the thickness of the substrate, t_f is the thickness of the film, R is

the radius of the curvature of the film on the substrate and R_b the radius of curvature of the bare substrate.

X-ray diffraction (XRD) was used to determine the preferred orientation of the AlN films. XRD data were collected using Cu Kα (1.5418 Å) radiation (40 kV, 40 mA), Bragg–Brentano geometry with 2 mm divergence slit and 0.05 mm receiving slit, graphite monochromator, $2\theta = 30°–80°$, step size 0.02° and counting time of 10 s per step. Peaks were identified using the JCPDS-ICDD x-ray database, no 25-1133, for aluminium nitride, hexagonal zincite structure.

Cross-sectional transmission electron microscopy (XTEM) was carried out on selected samples. The XTEM samples were thinned using a tripod polisher with diamond paper followed by ion beam thinning. A combination of electron diffraction and dark field imaging was used to examine the microstructure and to provide information concerning the preferred orientation in the film. The selected area diffraction patterns were taken using a circular aperture with a diameter of approximately 100 nm.

3. Results and discussion

The effects of energetic ion bombardment on a growing film are determined by the fraction of ions arriving with high energy and the value of that energy. The fraction of ions with high energy is determined by the duty fraction, $\boldsymbol{r}$, of the high voltage pulses. Many of the ions accelerated in a plasma sheath created by pulsed bias $\boldsymbol{V}$ arrive with less than their maximum energy, $\boldsymbol{qeV}$, where $\boldsymbol{q}$ is the mean charge state of the ions. A portion of the ions is accelerated across the plasma sheath during the rise and fall time of the pulses [4]. During the rise time (<1 μs), the sheath is still expanding and the majority of the ions with less energy than that corresponding to the full potential drop arrive at this time [4].

We make a simplifying assumption that the actual energy of the ions at implantation is proportional to the applied voltage, in which case the energy delivered is proportional to the quantity $\boldsymbol{qVr}$. Since the duty fraction $\boldsymbol{r}$ is given by the product of the pulse duration $\boldsymbol{\omega}$ and the frequency $\boldsymbol{f}$, we expect that the stress present in the film will be proportional to $\boldsymbol{qVf\omega}$, as noted in previous work [5]. In the current work, the pulse $\boldsymbol{\omega}$ was held constant at 20 μs, and since the charge state distribution is also expected to be constant the stress should only depend on the product $\boldsymbol{Vf}$.

The dependence of the stress on Vf is shown in figure 1. The results indicate that a maximum stress value of 4.34 GPa was obtained for a film prepared using Vf of 100 kV Hz ($V = 2$ kV, $f = 50$ Hz), the lowest value of Vf we applied in these experiments. With increasing Vf, the stress then decreases progressively until eventually it settles down to an average value of less than 0.50 GPa for Vf greater than 3000 kV Hz. The Vf values for these points were 3500 kV Hz ($V = 7$ kV, $f = 500$ Hz), 4500 kV Hz ($V = 9$ kV, $f = 500$ Hz), 5000 kV Hz ($V = 5$ kV, $f = 1000$ Hz) and 6400 kV Hz ($V = 8$ kV, $f = 800$ Hz).

The data have been fitted to two physical models and the resulting regression coefficients (R^2) and fitting parameters are shown in table 2. The first row shows the equation and fitting parameters for the exponential model, while the second row contains those for the percolation model. The exponential model is based on the assumption that stress relief occurs in small isolated volumes (thermal spikes) surrounding the impact sites of the energetic PIII ions. The relaxation that occurs in these thermal spikes leaves the affected pockets of the film with a much lower level of residual stress. We assume that it is not possible to relieve the stress completely (i.e. to 0 GPa) as some stress will remain at the thermal spike edges where atoms are not so mobile [6]. As the bias V increases, the volume of the thermal spikes associated with the energetic ion increases, and as the frequency f increases, the number of such spikes impacting

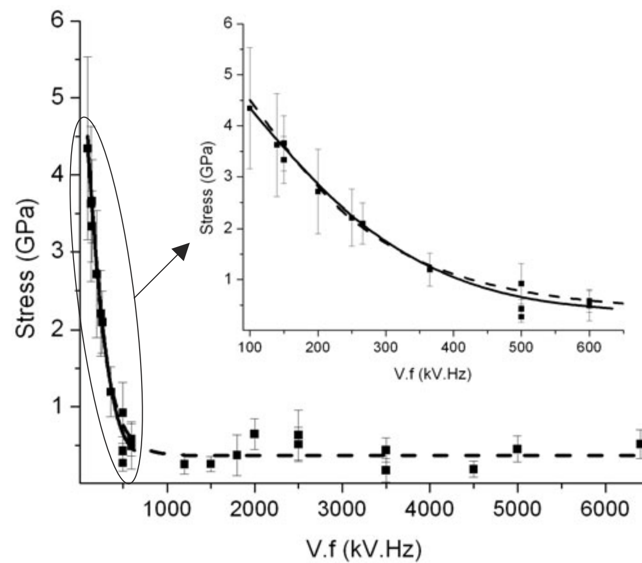

Figure 1. Residual stress in AlN versus the product of Vf. The lines of best fit are shown by the exponential model (dashed curve) and percolation model (solid curve). The inset shows an expanded region (Vf from 0 to 600 kV Hz) to highlight the differences between the two models.

Table 2. The fitting parameters for the exponential and percolation models.

Fitting equation (y = stress; $x = Vf$)	R^2 (no of free parameters)	a (GPa)	b (GPa)	c (V s^{-1})
$y = a + b\exp\left(\frac{-x}{c}\right)$	0.979 59 (3)	0.366 ± 0.056	7.497 ± 0.530	168.472 ± 13.565
$y = a + b(c - x)^T$ $3 < T < 4$	0.986 61 (3.5) $T \to 3$	0.421 ± 0.304	(0.154 ± 2.845)E-7	733.231 ± 507.393

on the film increases proportionally. As impact volume and number increase there will be overlap of impacts. Thus the volume of material relieved by each impact will be on average proportional to the remaining volume not yet treated with thermal spikes. The assumption that the stress remaining in the film is proportional to the volume fraction which has not been 'treated' by a thermal spike gives rise to an exponential relationship between stress and Vf. The percolation model is based on previous work on the 'Swiss cheese' model [7] for the dependence of the elastic modulus of a sheet on the fraction of circular holes drilled in the sheet, making the assumption that the thermal spike resulting from an ion impact relieves the stress in an approximately cylindrical region of the film. The physical interpretations of the adjustable or free parameters of these two models have been discussed in detail in previous work [5, 8].

The results in table 2 shows that the number of free parameters in the exponential decay model is three. The parameter a is the residual stress which cannot be relieved by high voltage pulse biasing, the parameter b is the difference between the maximum stress which would be attained without pulse biasing and the residual stress, and the parameter c represents $\frac{E_A}{qw}$, the scaling factor for the exponent (see [5]). Here E_A is the activation energy for atomic rearrangement leading to relaxation [5]. The number of free parameters in the percolation

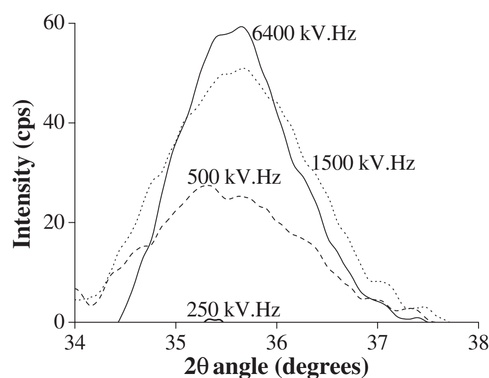

Figure 2. XRD plot of the (0002) reflection of AlN, collected using various Vf values.

model is shown as 3.5. This signifies the fact that three of the four parameters are free whereas the fourth, T, the critical exponent for the percolation process, is constrained to lie between 3 and 4. As shown by the arrow, the value attained by this parameter for the best fit is 3. Note that the percolation fit can only be applied to the points with $Vf < c$, where c is the percolation threshold, whereas the exponential model can be fitted over the whole data set. The parameters for the percolation model are not well determined by the fitting process. This indicates that there is some coupling between the parameters so that a change in one parameter can be compensated for by changes in the others. A larger data set is therefore needed to give better parameter determinations for the percolation model.

The lines of best fit are shown in figure 1 by a solid curve for the percolation model and a dashed curve for the exponential model. In the region of validity of the percolation model the two models are very close and can hardly be differentiated at this scale. The inset in figure 1 also shows this section of the plot expanded on the Vf axis to show the differences between the two models.

XRD data were collected for four samples and the results are shown in figure 2. The only peak observed in the XRD patterns is the (0002) reflection of zincite type AlN, showing that a preferred orientation of the crystallites occurs with the c axis perpendicular to the plane of the film. The (0002) reflection has the strongest intensity for the AlN film prepared using a Vf of 6400 kV Hz ($V = 8$ kV, $f = 800$ Hz). As the product of Vf is decreased, we observe a progressive reduction in intensity of the (0002) peak. At a Vf of 250 kV Hz ($V = 1.5$ kV, $f = 166$ Hz), the (0002) peak has nearly disappeared. These results show that a change is observed in the preferred orientation with changes in the implantation power, which is approximately proportional to Vf as discussed above.

Figure 3 shows a cross section viewed in the TEM and a selected area diffraction (SAD) pattern from the film prepared using a Vf of 6400 kV Hz ($V = 8$ kV, $f = 800$ Hz), with a stress value of 0.5 GPa. There are two strong spots corresponding to the (0002) diffraction spacing. This indicates that the majority of (0002) planes are oriented perpendicular to the line joining these spots. Thus the diffraction pattern indicates that the (0002) planes lie in the plane of the film so that the c axis is oriented perpendicular to the plane of the film. This is in agreement with the XRD results in figure 2.

Further cross section TEM images and SAD patterns were collected for three samples corresponding to Vf values of 1200 kV Hz ($V = 2$ kV, $f = 600$ Hz), 150 kV Hz ($V = 2$ kV, $f = 75$ Hz) and 100 kV Hz ($V = 2$ kV, $f = 50$ Hz). These are shown in figures 3–6 respectively. The diffraction patterns clearly show that the AlN film undergoes a change in

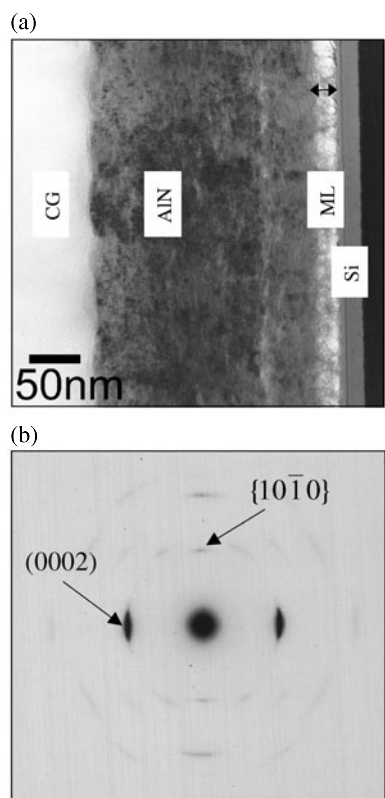

Figure 3. (a) Cross sectional view of a TEM sample deposited using a $Vf = 6400$ kV Hz ($V = 8$ kV, $f = 800$ Hz), stress = 0.50 GPa, and (b) its selected area diffraction (SAD) pattern. CG, carbon glue; ML, mixing layer. The SAD pattern in (b) has been aligned to the correct orientation with respect to the image in (a).

its preferred orientation with decreasing Vf and increasing stress. The diffraction pattern in figure 4 is similar to that in figure 3 and indicates that this film still has the c axis predominantly perpendicular to the plane of the film. Figure 5 shows a more mixed orientation with many new pairs of spots appearing, although the strongest spots on the (0002) ring still indicate a preference for the c axis perpendicular to the film plane. There is a dramatic change in preferred orientation for the film of highest stress as shown in figure 6. The strongest (0002) reflections are now positioned so that the line joining them lies in the plane of the film, indicative of (0002) planes perpendicular to this line and thus a c axis lying in the plane of the film, with free rotation in that plane and around the c axis. These two free rotations give rise to fainter arcs visible in the diffraction pattern. Another clear trend is in the degree to which the (0002) reflection is concentrated around the preferred direction. The films with high Vf of 6400 kV Hz (figure 3(b)) and intermediate Vf of 1200 kV Hz (figure 4(b)) show the most concentrated intensity around the preferred direction, while at a Vf of 150 kV Hz the intensity of the (0002) reflection has spread around the diffraction ring, indicating a lower tendency to preferred orientation.

Several authors have attempted to use energy minimization to explain the preferred orientation of thin films containing stress (see for example [9–12]). The total energy has contributions from the top surface, the bottom interface with the substrate and the bulk

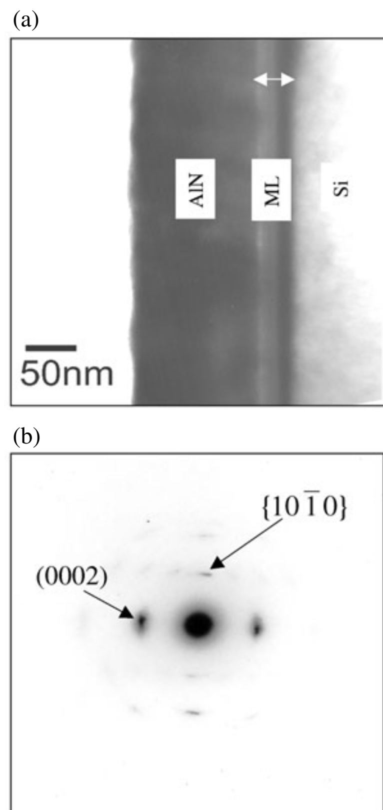

Figure 4. (a) Cross sectional view of a TEM sample deposited using a $Vf = 1200$ kV Hz ($V = 2$ kV, $f = 600$ Hz), stress = 0.25 GPa, and (b) its selected area diffraction (SAD) pattern. ML, mixing layer. The SAD pattern in (b) has been aligned to the correct orientation with respect to the image in (a).

strain energy. The preferred orientation in this approach is the one for which the total energy is a minimum. An alternative view is that dynamical effects associated with the interaction of the energetic beam of ions with the film material determine the preferred orientation [13]. Our results for preferred orientation are consistent with the observations of Clement *et al* [13] who studied rf sputtered AlN films at various deposition pressures. They found that at low sputtering pressures, where the most energetic bombardment occurs, corresponding to our high Vf films, the orientation was with the c axis normal to the film plane. For high sputtering pressures, corresponding to our low Vf case, the c axis was in the plane of the film.

In order to assist in the understanding of changes in preferred orientation observed experimentally, we calculate the surface energy of three important surface terminations of the AlN zincite structure. The energy per unit area of the three principal surfaces $\{11\bar{2}0\}$, $\{10\bar{1}0\}$ and (0001) were calculated using first principles methods based on density functional theory. The calculated surface energy is shown in table 3 [14]. The (0001) surface is polar, and has a very high energy and is not expected to be exposed because of this. The (0001) oriented regions are therefore likely to be terminated by surfaces other than (0001) planes. Since the remaining two surfaces are close in energy, we believe that surface energy does not play a major role in determining preferred orientation.

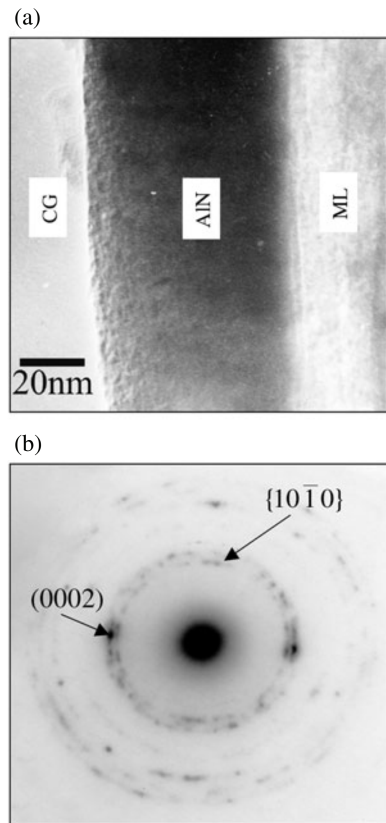

Figure 5. (a) Cross sectional view of a TEM sample deposited using a $Vf = 150$ kV Hz ($V = 2$ kV, $f = 75$ Hz), stress = 3.33 GPa, and (b) its selected area diffraction (SAD) pattern. CG, carbon glue; ML, mixing layer. The SAD pattern in (b) has been aligned to the correct orientation with respect to the image in (a).

Table 3. Surface energy values for AlN.

Principal surface	Surface energy (J m^{-2})
{11$\bar{2}$0}	3.21
{10$\bar{1}$0}	3.24
(0001)	15.80

We note that the ⟨0001⟩ direction has open channels along which ions can move relatively freely. A model has been developed for preferred orientation [15] based on molecular dynamics simulations of film growth in the presence of ion impacts. The degree to which the ion beam disordered the crystallites was lower for those crystallites oriented with a channelling direction aligned with the incident beam. The disordered crystallites grew at a lower rate than the aligned crystallites so that grain boundaries moved in favour of the aligned crystallites, leading to preferred orientation.

The energy minimization approach may predict a preferred orientation in which the *c* axis lies in the plane of the film under high stress conditions, depending on the values chosen for the elastic constants, as explained in our previous work on AlN prepared with DC bias [1].

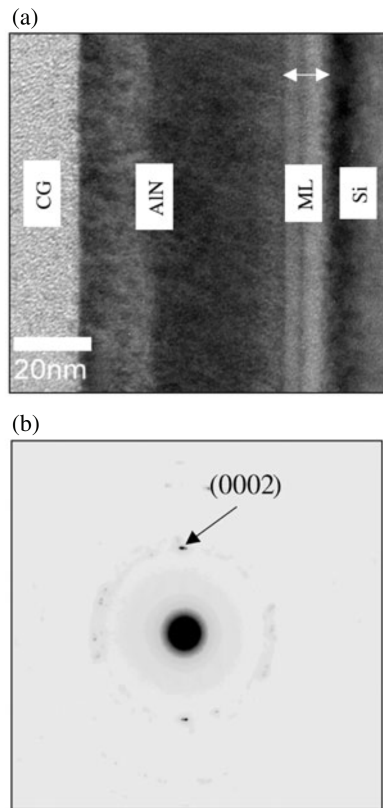

Figure 6. (a) Cross sectional view of a TEM sample deposited using a $Vf = 100$ kV Hz ($V = 2$ kV, $f = 50$ Hz), stress = 4.34 GPa, and (b) its selected area diffraction (SAD) pattern. CG, carbon glue; ML, mixing layer. The SAD pattern in (b) has been aligned to the correct orientation with respect to the image in (a).

This orientation is not explained by a mechanism based on dynamical interactions with the ion beam. However, we believe that only the dynamical model can explain the different degrees of preferred orientation found in films of low stress and low Vf as reported in [1] compared to films of similar stress at high Vf as reported in this paper.

4. Conclusions

Our results for the stress produced in AlN films subjected to pulsed bias show a universal dependence of the stress on the quantity Vf where V is the applied voltage and f is the frequency. The dependence is well described by an exponential fit over the whole data set or a percolation model over its region of applicability.

There is a strong tendency towards the development of the (0002) preferred orientation in low stress AlN films prepared with pulsed bias at high values of the applied bias–frequency product (Vf). This (0002) preferred orientation corresponds to the $\langle 0001 \rangle$ axis perpendicular to the film. This is consistent with models based on dynamical effects associated with the interaction with the incident ion beam. The strong tendency to preferred orientation with the $\langle 0001 \rangle$ direction lying in the film plane at high stress conditions is predicted only by energy minimization. Both ideas therefore are required to explain the orientation behaviour over the full range of PIII deposition conditions.

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