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The orientation dependence of elastic strain energy in cubic crystals and its application to the preferred orientation in titanium nitride thin films

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Abstract. Elastic strain energy under some conditions provides the major contribution to the total energy of a film growing on a substrate from condensing vapour. Polycrystalline films grown with intrinsic stress induced by energetic bombardment are expected to show orientations which minimize total energy. Even for a cubic crystal in a non-hydrostatic stress field the energy is a function of the relative orientation of the stress field and the crystallographic axes. The Gibbs free energy is minimized under constant stress and temperature conditions at thermal equilibrium. In this paper we derive expressions for the Gibbs free energy of a cubic crystal in uniaxial and biaxial stress fields and find the conditions under which it is a minimum. The sign of the expression $\delta = s_{11} - s_{12} - \frac{1}{2}s_{44}$ is the quantity which determines the behaviour of a cubic crystal and if negative, predicts that the [111] direction of the crystal will align with the principal stress of a uniaxial stress field and will lie normal to the plane of principal stresses in a biaxial stress field. Experimental evidence is presented which shows that titanium nitride, TiN, which has a negative value of δ , obeys these predictions. If δ is positive, then the [100] direction of the crystal obeys the above rules rather than the [111] direction.

1. Introduction

All crystalline materials are elastically anisotropic, even those of cubic symmetry. This anisotropy gives rise to an orientation dependence of the elastic strain energy of a crystalline substance when it is placed in a non-hydrostatic stress field. This effect is of special interest in thin-film growth, where atoms condense onto a substrate in such a way as to minimize the total energy of the system in the limited time during which the atoms are mobile before being frozen into a fixed position. In this paper we develop theory to enable the evaluation of the elastic strain energy in a two-dimensional or *biaxial* stress field for a cubic crystal and apply it to the case of a titanium nitride film. Titanium nitride is a cubic material, well studied in thin-film form because of its wear-resistant and decorative applications and often prepared under strong biaxial stress conditions. An aim of this work is to prove that the elastic strain energy for TiN is in fact a minimum when the [111] direction lies normal to the film, therefore explaining the commonly observed preferred orientation in this material.

The thermodynamics of elastic strain energy in crystalline structures has been discussed in the book by Nye [1]. The book by Khachatryan [2] contains examples of the application of thermodynamic theory to structural phase transformations and discusses examples of the *tweed* structure in alloys containing tetragonal precipitates. Elastic strain energy forms an important, but not the only contribution to the total energy of a film on a substrate. In this paper, however, we are interested in these cases where it is the dominant contribution. We

will first derive the conditions on the elastic constants of a cubic material which determine the orientation of the crystal axes relative to the stress field in order to minimize the elastic strain energy. We consider only uniaxial stress fields and biaxial stress fields where the principal stresses are equal. The link between preferred orientation in thin films and the presence of stress in the films has been noted in previous work [3, 4], but exact results for the case of a biaxial stress field are not currently available in the literature, to our knowledge. A number of investigations of the preferred orientation in thin films of titanium nitride have been carried out, but in order to compare the results with theory, the stresses present need to be characterized. To this end we have made a number of new measurements of the stress in TiN films deposited by an ion plating technique, have correlated them with the preferred orientation and have compared the results with theoretical predictions.

The origin of stresses in thin films is a subject about which much is known as a result of experimental observations as well as computer simulations using molecular dynamics techniques. The energy of the condensing species during a physical vapour deposition process is the most important single parameter which determines the level of built-in or intrinsic stress in the film. Growth at thermal energies of less than 1 eV generally produces films under tensile stress, while deposition at energies of some tens of eV generally produces films under compressive stress. Since the forces sustaining the stress in a thin film are applied by the substrate, it is expected that the stress field will be a biaxial one, or at least approximately so. Useful empirical theories to describe the energy dependence of the stress level in thin films have been developed by [5] and [6]. These reproduce the common experimental observation of a stress level which, with increasing energy, changes from tensile to compressive, reaches a maximum compressive value and with further increase in energy shows a steady decrease, while remaining compressive. The molecular dynamics work of [7] reproduces this behaviour and gives insights into the processes giving rise to stress. Equilibrium thermodynamics has a role to play in the study of film growth, as it enables the use of the large data base on the equilibrium properties of solids to be used to understand the results of film growth. At the outset, however, it must be understood that the processes occurring on short time-scales during film growth do not achieve thermal equilibrium, but that the direction in which the structures are evolving during the condensation process may be predicted by equilibrium thermodynamics.

The possibility that kinetic factors in film growth may be more important in determining preferred orientation than energy minimization has been raised recently [8] in connection with films grown under low-stress conditions. Under these conditions the films contain voids and show a pronounced columnar structure. It is conceivable that columns containing crystals will show different growth rates depending on the orientation of the crystals within them so that crystal orientations with high growth rates will become dominant. Here we are not concerned with cases where the films show columnar structure and associated void spaces, as we wish to discuss the case where elastic strain energy in the bulk is the main contribution to the total energy. The total energy will contain contributions from the surface energy of the free surface of the film and the interface energy of the film–substrate interface as well as from the elastic strain energy in the bulk. Columnar structure, if present, would result in a large surface energy contribution from the internal surfaces of the columns. In the limit of thick films under high levels of stress and not containing voids, the bulk elastic strain energy will become dominant and this is the case we wish to consider here. After discussing the case of a crystal of any symmetry in a general stress field in section 2, we consider the specific cases of a cubic crystal in uniaxial and biaxial fields. Finally, we consider the application to the problem of preferred orientation in titanium nitride thin films.

2. Gibbs free energy of a crystal in a stress field

The Gibbs free energy is the appropriate thermodynamic function for systems at constant temperature and constant pressure. In cases where the applied stress is not hydrostatic pressure, but a general stress field, the Gibbs free energy may be generalized following Nye [1] to

$$G = U - \sum_{i,j} \epsilon_{ij} \sigma_{ij} - TS \quad (1)$$

where U is the internal energy, S the entropy, T the temperature and ϵ_{ij} is the strain tensor of the substance. The differential change in G is

$$dG = dU - \sum_{i,j} \epsilon_{ij} d\sigma_{ij} - \sum_{ij} d\epsilon_{ij} \sigma_{ij} - T dS - S dT. \quad (2)$$

At constant temperature,

$$dG = - \sum_{i,j} \epsilon_{ij} d\sigma_{ij} \quad (3)$$

using the first law of thermodynamics to cancel some terms. It is convenient to write the stress tensor as the product of a scalar magnitude and a tensor with a constant trace of order unity so that, for example, the differential tensor $d\sigma_{ij}$ is written $\hat{\sigma}_{ij} d\sigma$ so that

$$dG = - \sum_{i,j} \epsilon_{ij} \hat{\sigma}_{ij} d\sigma = - \sum_{i,j,k,l} s_{ijkl} \hat{\sigma}_{ij} \hat{\sigma}_{kl} d\sigma \quad (4)$$

where s_{ijkl} is the elastic compliance tensor which has a form determined by the symmetry of the crystal. The Gibbs free energy is assigned the value G_0 at a datum condition of the substance at a convenient temperature T_0 and convenient stress level. The datum stress level is conveniently taken as zero. To find G at a given stress level σ we integrate the stress from zero to σ :

$$G = G_0 + \int_0^\sigma dG = G_0 - \frac{1}{2} \sigma^2 \left(\sum_{i,j,k,l} s_{ijkl} \hat{\sigma}_{ij} \hat{\sigma}_{kl} \right). \quad (5)$$

It is convenient to use a notation in which the fourth-rank compliance tensor is replaced by a 6×6 matrix and the second-rank stress tensor by a 1×6 vector. We can then write the expression for the Gibbs free energy in matrix form as

$$G = G_0 - \frac{1}{2} \sigma^2 [\hat{\sigma} \mathbf{s} \hat{\sigma}^T]. \quad (6)$$

For a cubic substance, the compliance matrix \mathbf{s} is

$$\begin{pmatrix} s_{11} & s_{12} & s_{12} & & & \\ s_{12} & s_{11} & s_{12} & & & \\ s_{12} & s_{12} & s_{11} & & & \\ & & & s_{44} & & \\ & & & & s_{44} & \\ & & & & & s_{44} \end{pmatrix}. \quad (7)$$

3. A cubic crystal in a uniaxial stress field

For a uniaxial stress with forces exerted parallel to the x -axis (the crystallographic [100] direction), the stress tensor expressed as a 1×6 vector has the form $\hat{\sigma}' = [1, 0, 0, 0, 0, 0]$ and the Gibbs free energy reduces to the simple form

$$G_{100} = G_0 - \frac{1}{2}\sigma^2 s_{11}. \quad (8)$$

For a general orientation of the stress relative to the crystallographic axes, the stress tensor $\hat{\sigma}$ may be rotated in three dimensions into a new stress tensor $\hat{\sigma}'$ using a rotational transformation. This rotation is specified by the matrix a_{ij} .

The Gibbs free energy of the crystal under the rotated stress field is

$$G = G_0 - \frac{1}{2}\sigma^2 [\hat{\sigma}' \mathbf{s} \hat{\sigma}'^T] \quad (9)$$

where $\hat{\sigma}' = [a_{11}^2, a_{21}^2, a_{31}^2, a_{31}a_{21}, a_{31}a_{11}, a_{21}a_{11}]$ and T denotes the transpose. This form for $\hat{\sigma}'$ is satisfied in eight different ways, corresponding to the eight symmetry-equivalent stresses:

$$\hat{\sigma}' = [\sigma'_1, \sigma'_2, \sigma'_3, \pm\sqrt{\sigma'_1\sigma'_2}, \pm\sqrt{\sigma'_3\sigma'_1}, \pm\sqrt{\sigma'_2\sigma'_1}] \quad (10)$$

where the σ'_i are the diagonal components of $\hat{\sigma}'$. G has the same value for each of the eight possible choices of sign for the last three entries in (11), and has the value

$$G = G_0 - \frac{1}{2}\sigma^2 \left[s_{11}(\sigma_1'^2 + \sigma_2'^2 + \sigma_3'^2) - 2\left(s_{11} - s_{12} - \frac{1}{2}s_{44}\right)(\sigma'_1\sigma'_2 + \sigma'_2\sigma'_3 + \sigma'_3\sigma'_1) \right]. \quad (11)$$

Since the trace of the stress tensor is invariant under rotation and is equal to unity:

$$G = G_0 - \frac{1}{2}\sigma^2 \left[s_{11} - 2\left(s_{11} - s_{12} - \frac{1}{2}s_{44}\right)(\sigma'_1\sigma'_2 + \sigma'_2\sigma'_3 + \sigma'_1\sigma'_3) \right] \quad (12)$$

this can be written as a sum of orientation-independent and orientation-dependent terms

$$G = G_0' + \sigma^2 \left(s_{11} - s_{12} - \frac{1}{2}s_{44} \right) C. \quad (13)$$

The quantity G_0' is orientation independent while the quantity

$$C = \sigma'_1\sigma'_2 + \sigma'_2\sigma'_3 + \sigma'_1\sigma'_3 \quad (14)$$

contains the orientation dependence. C has a minimum value of zero when the uniaxial stress is aligned with a [100] direction and a maximum value of $\frac{1}{3}$ when it is aligned with a [111] direction. If the value of $\delta = s_{11} - s_{12} - \frac{1}{2}s_{44}$ is less than zero, then G will be minimized when the stress is aligned with a [111] direction; when δ is positive, G will be minimized when the stress is aligned with a [100] direction. This result is closely related to that for the orientation dependence of Young's modulus in a cubic material. If the quantity δ is positive, then the Young's modulus is minimum along [100] and maximum along [111] and vice versa when δ is negative [1]. It is then intuitively expected that the elastic energy will be minimized when the most compliant direction of the crystal is aligned with the stress axis, as the above result for G shows. For titanium nitride, the quantities s_{11} , s_{12} and s_{44} are known (see table 1) and, in common with other materials with the rock-salt crystal structure, has a negative value of δ . Therefore in a uniaxial stress field, the [111] direction of the TiN crystal should align with the stress axis.

Table 1. Values of the components of the elastic compliance tensor s_{ij} .

Compliance	Value (GPa)
s_{11}	2.17×10^{-3}
s_{12}	-0.38×10^{-3}
s_{44}	5.95×10^{-3}

4. A cubic crystal in a biaxial stress field

For a biaxial stress field with equal principal stresses applied in the x - y plane the stress tensor may be expressed as the sum of a hydrostatic pressure and a negative uniaxial stress along the z -axis, thus:

$$\boldsymbol{\sigma}_b = \boldsymbol{\sigma}_h - \boldsymbol{\sigma}_z \quad (15)$$

where the stress tensors are respectively biaxial, hydrostatic and uniaxial along z . This decomposition is readily seen when the tensors are written out in full

$$\begin{pmatrix} 1 & & \\ & 1 & \\ & & 0 \end{pmatrix} = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} - \begin{pmatrix} 0 & & \\ & 0 & \\ & & 1 \end{pmatrix}. \quad (16)$$

We wish to evaluate the Gibbs free energy as a function of the orientation of the crystal axes and the principal stress plane. Writing the Gibbs free energy in terms of the rotated tensor as before,

$$G = G_0 - \frac{1}{2} \sigma^2 [(\boldsymbol{\sigma}'_h - \boldsymbol{\sigma}'_z) \mathbf{s} (\boldsymbol{\sigma}'_h - \boldsymbol{\sigma}'_z)^T] \quad (17)$$

$$G = G_0 - \frac{1}{2} \sigma^2 [\boldsymbol{\sigma}'_h \mathbf{s} \boldsymbol{\sigma}'_h{}^T + \boldsymbol{\sigma}'_z \mathbf{s} \boldsymbol{\sigma}'_z{}^T - \boldsymbol{\sigma}'_h \mathbf{s} \boldsymbol{\sigma}'_z{}^T - \boldsymbol{\sigma}'_z \mathbf{s} \boldsymbol{\sigma}'_h{}^T]. \quad (18)$$

The first term in brackets is not dependent on the orientation of the stress field relative to the crystallographic axes, since $\boldsymbol{\sigma}_h$ is a unit tensor invariant under rotation. This corresponds to the fact that the strain energy of a specimen under hydrostatic stress does not depend on orientation. The last two terms also can be shown to be independent of orientation and can be combined with the first term. Doing this, we have

$$G = G_0 - \frac{1}{2} \sigma^2 [(s_{11} + 2s_{12} + \boldsymbol{\sigma}'_z \mathbf{s} \boldsymbol{\sigma}'_z{}^T)]. \quad (19)$$

The only orientation dependence occurs in the last term in the brackets, and the orientation dependence of this is already known from the previous section. Depending on the sign of δ the value of G will be minimized when either the crystal [111] or [100] directions are aligned with the uniaxial stress. Since the uniaxial stress is normal to the plane containing the biaxial stresses, this means that, for δ negative, the [111] direction will lie normal to the biaxial stress plane and for δ positive, the [100] direction will lie normal to the biaxial stress plane, in order to minimize G .

5. Application to preferred orientation in TiN

In this section, the above theoretical treatment will be applied to the case of TiN thin films. TiN thin films of stoichiometric composition were grown using an ion plating technique which has been described in detail elsewhere. The stress is induced by biasing the substrate

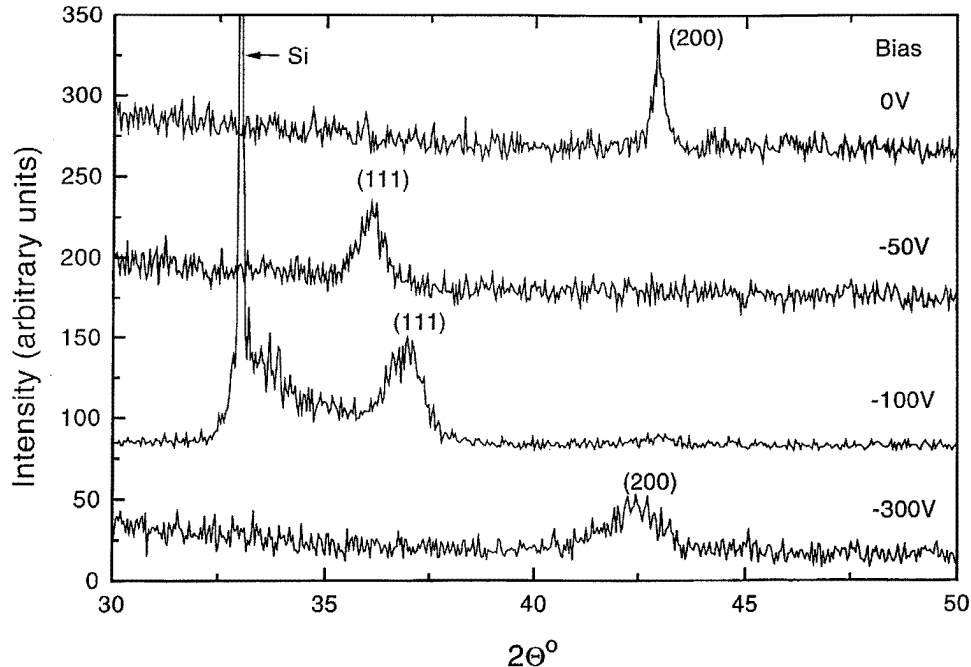


Figure 1. The x-ray diffraction intensity as a function of scattering angle 2θ in degrees for TiN films prepared at four different bias voltages applied during deposition. The films prepared at 0 V and -300 V bias show [100] preferred orientation and the remainder show [111] preferred orientation.

negative so that ions are accelerated onto the growing surface of the film. The level of compressive biaxial stress could be controlled over a wide range by adjusting the bias potential resulting from the application of rf power to the substrate table. The stress was measured by first determining the curvature of the silicon wafer substrate resulting from the stress in the film and then calculating the stress using the Stoney equation [9]. The value of the stress was found to be compressive and to depend on the energy of the bombarding ions in the expected fashion, as shown in table 2. The preferred orientation of the polycrystalline film was examined using both electron and x-ray diffraction techniques. For electron microscopy, the films were prepared on sodium chloride substrates so that they could readily be transferred to electron microscope grids. Electron diffraction patterns were acquired using 300 keV electrons in an electron microscope and were obtained by scanning the diffraction pattern from a selected area of the film over the entrance aperture of an electron energy-loss spectrometer. When the electrons are at normal incidence to the film, those Bragg planes lying normal to the film surface are in the reflecting position. The specimen was tilted 50 degrees away from the beam direction to bring Bragg planes lying at large angles to the film surface into the reflecting position. For x-ray diffraction studies, the films were prepared on silicon wafer substrates. The 2θ scans were run on a powder diffraction camera so that Bragg planes parallel to the substrate surface were in the reflecting position.

The results are entirely consistent with theory for a cubic substance with a negative value of the parameter δ . At low values of the stress, the preferred orientation is with [100]

Table 2. The dependence of the compressive biaxial stress in thin films of TiN as a function of the bias voltage applied to the substrate. The bias voltage directly determines the energy of the bombarding ions.

Bias (V)	Stress (GPa)
0	0.1
50	5.0
100	1.5
300	0.6

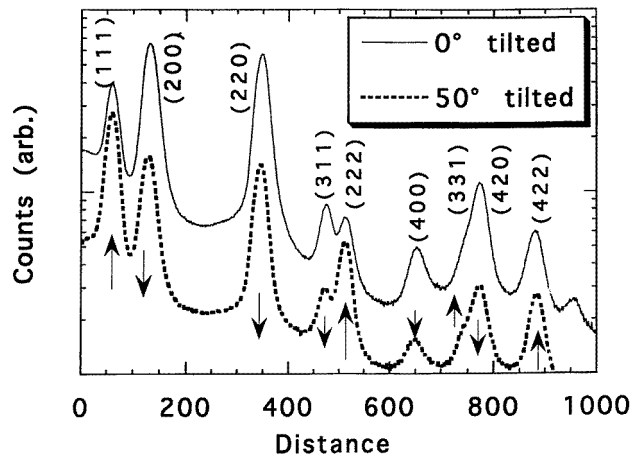


Figure 2. Electron diffraction intensity as a function of distance across the diffraction pattern. The solid curve is for normal incidence and the dotted curve is for the film tilted at 50 degrees to the electron beam. In the latter case, the diffraction intensity is measured across the diffraction pattern in the direction of the film normal.

normal to the film surface. The surface energy of the [100] surface is lower than that of the other low-index faces of TiN [8] and therefore in the absence of a large contribution from the bulk elastic energy, the surface energy will dominate. This situation applies at low energies of bombardment (0 V bias) as well as at high energies of bombardment (−300 V bias). At intermediate energies (−50 V and −100 V bias) the large compressive stresses give rise to a large bulk strain energy contribution which causes the [111] direction to lie normal to the plane of the biaxial stress. The x-ray diffraction patterns at three different bias levels are shown in figure 1, and show the sequence of orientation changes with increasing bias voltage. The position in 2Θ of the [111] reflection in the specimens at bias levels of −50 V and −100 V is due to the effect of the biaxial stress causing an expansion normal to the film plane. The electron diffraction patterns shown in figure 2 for the film at −100 V bias show the effect of tilting the specimen. At normal incidence the [111], [200], and [220] reflections are all observed. For [111] strictly normal to the film, the [111] and [200] reflections should not be observed but will be observed if some misorientation is allowed. This is likely to occur in practice, as the energy penalty for slight misorientation is not large enough to prevent it. As the film is tilted, the diffraction pattern shows a changes in the diffraction rings. The [111] ring shows pronounced arcs of high diffraction intensity corresponding to diffraction from the [111] planes normal to the surface and also from the

other [111] planes of crystallites constrained with a [111] direction normal to the surface. Scans shown in figure 2 are for the electron beam at normal incidence to the film and for the specimen tilted at 50 degrees to the beam.

The scan at the 50-degree tilt passes through the diffraction pattern in a direction normal to the film and therefore includes the strong [111] arcs. In summary, the electron diffraction pattern is consistent with a preferred orientation in which the [111] directions of the crystallites are constrained to be normal to the film but otherwise all possible orientations are allowed. This type of orientation is exactly that predicted by the theory.

6. Conclusion

The type of preferred orientation occurring in thin films grown under conditions in which high stress levels are generated can be predicted by an equilibrium thermodynamic theory in which the Gibbs free energy is minimized. For cubic crystalline substances the parameter $\delta = s_{11} - s_{12} - \frac{1}{2}s_{44}$ determines the type of behaviour expected. In the case of $\delta < 0$, in a biaxial stress field, the Gibbs free energy is minimized when the [111] direction is normal to the stress plane. In the case $\delta > 0$ the [100] direction is normal. The predictions are in complete agreement with the observed type of preferred orientation in TiN films grown with ion-bombardment-induced compressive stress.

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