A PHYSICAL BASIS FOR STRESS REDUCTION DURING ION BEAM ASSISTED DEPOSITION

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Introduction

Deposition of thin films and ion implantation in solids have been actively pursued as a means of enhancing surface properties. Conventional thin films often suffer from stresses which limit their mechanical integrity (1). Ion implantation has a limitation in terms of the depth to which the surface region is influenced. Ion beam assisted deposition (IBAD) which began with the work of Hirsch and Varga (2) has been shown to avoid these disadvantages by the simultaneous use of deposition and ion bombardment techniques. Although there are many possible benefits of using IBAD (3,4,5), we will be concerned here primarily with reduced stresses. Attempts have been made to explain the process involved but a full understanding is yet to emerge. In this work we show for the first time that the stress that tends to appear in a growing film will influence the microstructural evolution caused by ion bombardment in a manner that causes the stress to reduce.

Origin and Effect of Stresses

A film grown without bombardment at its surface can exhibit stresses of various kinds (1). If the coefficients of thermal expansion of the film and substrate materials are very different, the film may develop a stress in cooling from the deposition temperature. This kind of stress is termed extrinsic stress. Another kind of stress, termed intrinsic stress, can be of greater importance, as with hard metal films. It is believed that this may arise as follows. When a layer of film atoms has just condensed, the atoms in this layer are in a state of disorder and begin to order. However for this to happen, the layer must shrink. Since it is constrained by the underlying layers, a tensile stress develops.

We now consider the effect of ion bombardment and the role played by stresses. Ion bombardment produces interstitials and vacancies. For metal films at temperatures of interest in the present context, interstitials are mobile and the vacancies are immobile (6). Those vacancies that are not annihilated will tend to produce a negative volume change which is isotropic. The interstitials that are not annihilated will cluster to form discs (dislocation loops) which would tend to produce a positive volume change. Ordinarily, there should be no net change. However in the case of a metal film which develops a tensile stress for the reason mentioned above, the interplanar spacing is wider than normal for vertical planes and, due to the Poisson effect, smaller than normal for the horizontal planes. A similar stress situation has been considered previously in connection with the irradiation creep of reactor wall materials (7). Loops nucleate preferentially with their normal aligned parallel to an applied tensile stress (they find more space between adjacent planes and so nucleation is easier). This effect was termed Stress Induced Preferential Nucleation (SIPN). In our situation, the stress is internal but will serve to induce preferential nucleation just the same. Thus, the tendency of the interstitial loops to produce growth will be larger in the plane of the film than in the vertical direction. The vacancies cannot therefore compensate the lateral tendency (they will overcompensate the
vertical tendency). Since the film is constrained by the substrate, the effect will be a reduction in tensile stress instead of growth. It has been shown in irradiation studies that the number of loops stops increasing after a short nucleation stage (8). Thereafter, the growth of loops would cause the stress reduction to continue. This continued effect should be independent of the (reducing) value of the stress except that there is a further addition to this effect arising from the fact that the aligned loops grow faster than the unaligned ones (Stress Induced Preferential Absorption, or SIPA). This additional effect of course reduces as the stress reduces. The concepts just discussed are important since it has been shown that stress reduction during IBAD is not an implantation effect (5).

Mathematical Formalism

It is easily shown that the displacements per atom (d.p.a.) in a film growing by IBAD is given by:

$$d.p.a. = \frac{v_s \Phi}{Nr}$$

(1)

where $v_s$ is the number of vacancies created by one ion, $\Phi$ is the ion flux, $N$ is the atomic density, and $r$ is the growth rate of the film. The time that any point experiences displacements is the time taken to build up a film thickness equal to the projected range, $R_p$, of the ions, at the bombarding energy. As a consequence it will be seen that the average damage rate (d.p.a.s$^{-1}$) is given by:

$$d.p.a.s^{-1} = \frac{v_s \Phi}{NR_p}$$

(2)

However the damage rate at the surface is more important than the average value since it determines the loop density $N_l$ (the nucleation stage is short). The surface value will depend on the rate of energy loss at the surface and of course the ion flux.

We now consider a polycrystalline metal film of cubic structure (such as chromium). Such films tend to be textured such that low index planes have a simple orientation with respect to the plane of the film (9). Loops can form in an orientation such that they form planes that lie parallel to one of the cube faces. There are two orthogonal sets of such planes for which the normal may lie in the plane of the film. The planes in these two sets are the preferred planes. Following Bullough (7), the excess fraction, $f$, of loops which nucleate as one such set of planes is given by:

$$f = \frac{\exp\left(\frac{p_o n b^3}{kT}\right) - 1}{2\exp\left(\frac{p_o n b^3}{kT}\right) + 1}$$

(3)

where $p_o$ is the intrinsic tensile stress that would develop in the absence of ion bombardment, $n$ is the number of interstitials in an embryonic cluster at the instant it changes into a loop-shaped nucleus, $b$ is the magnitude of the Burgers vector, $T$ is the absolute temperature and $k$ is the Boltzman constant. It has been shown by computer simulation studies that $n$ has a value of around 10.

As is shown later, the high intrinsic stress that tends to develop in films grown at low substrate temperatures give values of $f$ close to 0.5 which means that nearly all loops nucleate in sympathy with the stress. In this limit SIPA is unimportant and we can work on the basis of SIPN alone. There is a positive linear strain introduced in the plane of the film by each set of loops growing in parallel alignment. The number of such loops is the sum of the number of those that form randomly and the number of those that form in sympathy with the stress. This number enables us to calculate the contribution to the strain on
account of the interstitial loops. From this we subtract out one-third of the volume strain created by the vacancies. Accordingly, the linear strain change, $\Delta \epsilon$, in the plane of the film is given by:

$$\Delta \epsilon = \left[ \frac{1}{3} (1 - 2\nu) N_f + \frac{1}{3} N_v \pi r_i^2 b \right] \left( 1 - \nu \right),$$

where $r_i$ is the loop radius and it can be shown that the factor $(1-\nu)$, where $\nu$ is the Poisson ratio, represents the Poisson effect of one set of planes on the other. Equation (4) simplifies as:

$$\Delta \epsilon = \frac{1}{3} N_f \pi r_i^2 b (1-\nu).$$

The calculation of $r_i$ can be calculated using rate theory (10) and one obtains:

$$r_i = \left[ \frac{d.p.a.}{\pi N_f} \right].$$

Equations (1), (3), (5) and (6) may be used to calculate the ratio $\phi/r$ (or in turn the ion-atom ratio, $\phi/rN$) at which $\Delta \epsilon = \rho E$, where $E$ is the elasticity modulus, in order to obtain the condition for zero stress.

**Comparison with Experiment**

In order to make comparisons with IBAD experiments, we first obtain some relevant data from the literature. Table I shows the value of intrinsic stress in chromium films deposited at two substrate temperatures in experiments that did not employ ion beams (11). The corresponding strain was calculated using a value of $10^9$ dynes/cm$^2$ for the elasticity modulus following Janda (9). The value of $f$ in each case works out to be 0.5 as listed, indicating that complete alignment would occur in an IBAD experiment even at the higher temperature.

<table>
<thead>
<tr>
<th>Substrate Temperature ($^\circ$K)</th>
<th>Stress (dynes/cm$^2$)</th>
<th>Strain</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.45X10$^{10}$</td>
<td>0.015</td>
<td>0.5</td>
</tr>
<tr>
<td>573</td>
<td>0.75X10$^{10}$</td>
<td>0.008</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Next we calculate the number of vacancies created per ion for argon ions bombarding chromium using TRIM 91.04, for various energies in the range 1 keV to 20 keV. (Each simulation was carried out for 300 ions). Fig. 1 shows that this turns out to be a nearly linear dependence. This is a direct consequence of the fact that the electronic energy loss is small, varying from $1/10$ (at the lowest energy) to $1/5$ (at the highest energy) of the nuclear energy loss. Equation (1) then implies that the ratio of arriving ions to depositing atoms required to produce a given d.p.a. will be nearly inversely proportional to energy and therefore so will be the ratio required to produce a certain stress reduction provided loop density does not vary significantly with energy and we confine ourselves to a fixed flux.

The values of nuclear energy loss vary slowly with energy (slower than $E^{1/2}$) as can be seen using TRIM calculations. Loop density varies slowly with the net nuclear energy loss or d.p.a.s$^{-1}$ (8). Further, it can be seen from equations (5) and (6) that the ultimate dependence of $\Delta \epsilon$ on loop density is small.
Thus, the present model predicts an essentially $E^{-1}$ dependence of the ion-atom ratio required to produce a given stress reduction. This dependence on energy is in accordance with the experimental results of Wolf and coworkers (4) who plotted the ion-atom ratio required to eliminate stress, as a function of the ion energy when the substrates were water cooled. A quantitative comparison will require calculation of the loop density as a function of the ion flux and this will be the subject of future work. Meanwhile, fig. 2 shows the ion-atom ratio required to achieve zero stress as a function of the ion energy for the two different substrate temperatures of table I when the value of loop density is chosen to be $3.5 \times 10^{19}$/cm$^3$ in order to match the 300°K curve to the data of Wolf.

**Concluding Remarks**

The present model can potentially be used to predict several features observed in IBAD experiments. Once the ion-atom ratio is increased to the point that tensile stress is eliminated, further increase can result in compressive stress since further growth of loops will have this result. Such an effect has been observed experimentally (4,5). If the film tends to contain voids or gaps at grain boundaries, sideways creep will result and close these spaces. Since the phenomenon described here depends on the orientation of the planes, on which loops form, with respect to the stress direction, some grains will be affected more than others resulting in texturing. It can also be understood that stress reduction is not effective at high substrate temperatures - the orientation of loops is increasingly thermally randomized.

There has been a previous effort to seek energy dependence criteria which would determine whether the phenomenon of IBAD is due to bombardment effects in the layer depositing at the surface or due to bombardment effects all the way down to the bottom of the ion range (3). The present study points out that first, one must have regard to the relative magnitude of electronic energy loss. If the electronic energy loss is negligible and the effects are of a bulk nature then the solution to the problem is simple - the dependence is $E^{-1}$ since all the energy goes into producing modification. Secondly, there can be a combination of both surface effects (in terms of a distinct stage early in the development of microstructure) and bulk effects. In the case analysed here, the energy dependence of the bulk effects is dominant and so the dependence is $E^{-1}$ again.

**References**

The number of vacancies created per ion as a function of ion energy for argon ions incident on chromium (obtained from TRIM calculations).

The critical ion-atom ratio (condition for zero stress) as a function of ion energy for argon ion assisted chromium deposition at two substrate temperatures. The experimental data of Wolf are also shown for comparison.