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Influence of thermal spikes on preferred grain orientation in ion-assisted deposition

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Theoretical models are presented to explain how thermal spike processes can induce the development of preferred orientation of polycrystalline grains during ion-assisted atomic deposition and thin film growth. Two ion energy regimes are investigated. In the first, higher-energy regime, ions penetrate growing grains and generate defects at rates dependent upon the probability of ion channeling in individual grains. The volume free-energy density of different grains is, therefore, different and the thermal spike arising from each ion impact results in preferential growth of grains with the lowest volume free-energy density. In the second, lower-energy regime, ions do not penetrate nor create defects in grains but the ion-induced thermal spikes centered on the surface can enhance surface atomic migration and lead to preferential growth of grains with the lowest surface free-energy density. The results in these two regimes are compared with the predictions of a model for preferred grain orientation evolution in the absence of ion assistance and where minimization of surface free-energy density is the driving process. Ion energy, ion flux density, depositing atom flux density, and system temperature conditions are established where ion-assisted and non-ion-assisted rates of preferred grain orientation become comparable. It is shown that, in general, the tendency toward preferred orientation is not a simple function of the energy per deposited atom.

I. INTRODUCTION

As polycrystalline thin films, grown by a variety of methods, thicken, they are usually observed to develop at least some degree of crystallographic texture and grains with preferred orientation dominate. Frequently, this corresponds to a fiber texture in which the surface normals to the grains become increasingly more nearly parallel to a specific crystallographic direction (out-of-plane texture) while the in-plane texture can remain more nearly random. Such textures are commonly observed in polycrystalline thin films grown by physical vapor deposition methods[1–5] and it is often observed that face-centered cubic (fcc) metal films exhibit a preferred $\langle 111\rangle$ orientation while body-centered (bcc) films exhibit a preferred $\langle 110\rangle$ orientation.

At lower temperatures, where the surface mobility of deposited atoms will be small and atomic migration between grains will be restricted, it has been suggested that the origin of the preferred texture is a ‘‘survival of the fastest’’ mechanism[6] in which grains with their direction of maximum growth speed normal to the surface outgrow grains of lower speed. This approach has been successfully modeled analytically[7–9] and by computer simulation.[7,8,10–15] At higher temperatures, where intergranular surface atomic migration increases, it is believed that preferred texture results from an attempt of the system to minimize surface free-energy density;[16] the planes normal to the crystallographic directions described above are those of minimum surface free-energy density for the respective crystallographic structures. This approach has also been successfully modeled analytically[17,18] and by simulation methods.[17–19]

In recent years there has been increasing interest in employing simultaneous ion bombardment of growing films using plasma sources,[20] separate ion fluxes,[21–23] or indeed using only low-energy ions[24,25] as the deposit species to modify film structure and properties. Additionally there has been some substantial investigation of the modification of film texture by postdeposition ion bombardment of grown films,[26–48] and again it has frequently been observed that the ion irradiation tends to promote a preferred grain orientation habit, although this may not necessarily be the same as that which is developed in the non-ion-bombardment-mediated conditions. In the case of congruent deposition and ion irradiation there has been one analytical model proposed by Bradley, Harper, and Smith[49] to explain the grain orientation preference phenomenon, which is based upon the knowledge that ions incident close to parallelism with open crystallographic directions are channeled into grains and, because they deposit less energy close to the surface than when incident in random directions, sputter these open surfaces less rapidly. Consequently these more open surface grains dominate the evolving film structure. Dong and Srolovitz[50,51] have recently used molecular dynamics simulation methods to study the evolution of grain orientation during simultaneous deposition and ion irradiation and have demonstrated that the channeling process is indeed the factor responsible for the grain reorientation but that the differential sputtering rate between grains is not the dominant process. Instead, it was observed that channeling reduces the ion-bombardment-induced bulk defect production and survival rates and hence the volume free-energy density is less enhanced in grains where channeling is important. The system is then driven toward minimum volume free-energy conditions, and it was suggested[51] that the thermal spikes that expand following the quench of the ballistic collision phase between ions and atoms and between atomic recoils aid this driving process. This proposal is synonymous with suggestions made by Van Wyk and Smith[27] to explain grain reorientation during postdeposition ion bombardment studies.

In this area of postdeposition ion bombardment there have also been essentially two analytical approaches to grain growth rather than preferred orientation. In the model proposed by Atwater, Thompson, and Smith,[40] ion irradiation is considered to generate point defects, and it was suggested that grain boundary motion resulted from either vacant site production followed by thermal atomic migration to the vacant site or collisionally induced vacancies and interstitials mutually annihilating. Such a model predicts a linear dependence of grain boundary expansion rates upon both the incident ion flux density and the elastic energy deposition density per ion and an approximately hyperbolic dependence on the cohesive energy of the deposited material. Such a model cannot adequately describe the large differences in observed grain growth rate for materials such as Pt and Au,[35] for which the ballistic collisional and defect production rates should be similar, nor the superlinear dependencies of growth rate upon elastic energy deposition density and reciprocal cohesive energy.[34,35,52] Such observations led Liu[52] and Liu, Li, and Mayer[38] to propose that it was the thermal spikes following the displacement events that enhanced surface atomic migration and grain growth and, subsequently, Alexander and Was[48] extended these arguments more quantitatively. In particular, these latter authors proposed that the force that drove grain expansion was the additional free-energy density associated with grain-boundary curvature (the well-known Gibbs-Thompson effect[53]).

It is clear from the above summary that thermal spike effects have begun to assume a central role in the explanation of grain evolution processes but, in the case of preferred grain orientation, the proposals remain qualitative. The present work advances an analytic approach to the role of thermal spikes in enhancing grain reorientation in ion-assisted atomic deposition in, essentially, two ion energy regimes. In the first, higher-energy regime, ions are considered to penetrate grains and cause differential defect production and survival rates and densities according to the extent of channeling in individual grains, and grain evolution is driven by the attempt to minimize volume free-energy density.[51] In the second, lower-energy regime, ions do not penetrate grains but deposit a fraction of their energy at the surface, which enhances surface atomic mobility and the system tends toward one of minimum surface free-energy density. The approximate magnitudes of grain reorientation rates are compared to estimates of rates when ion bombardment is absent[17] and the dependencies of the former rates upon the parameters of ion energy, ion and atom arrival rates, and system temperature are derived. It is demonstrated that the energy per deposited atom is not a single specific indicator of the tendency to grain orientation, and that, for lower-energy ions, the effect of simultaneous ion irradiation can enhance normal thermal processes but, for higher ion energies, irradiation-induced and thermally driven mechanisms may be competitive. The dominant effect depends on the magnitudes of the process parameters described above.

In the following section the basic equation for grain growth in the presence of a driving force and under constant temperature conditions is first reiterated and then relevant effects of ion bombardment on materials are briefly summarized. In particular, the production of defects during film growth is considered, including the effects of the channeling process on defect production rates, and the nature of the thermal spikes that occur following the quenching of ballistic collisional processes is examined. Such spikes induce spatiotemporal variations in local temperature, and in the third section it is demonstrated how these variations modify the grain growth rate equation. In the higher-energy regime, where defects are produced in the bulk of grains, two forms of spike are studied, the spherical spike that occurs when ions only just penetrate into grains and the cylindrical spike that occurs for deeper penetration. In the lower-energy regime, where no ion penetration occurs and bulk defect production is minimal, only the (hemi)spherical spike is relevant. In the former regime the modifications to volume free-energy density drive grain reorientation processes whereas in the latter regime modification of surface atomic mobility and differences in surface free-energy density drive grain reorientation.

In this discussion the behavior of only two neighboring grains is evaluated, but in the fourth section the analysis is generalized to determine the evolution of grain orientation preference from an initially random orientation distribution. This analysis follows a summary of the approach of Knuyt *et al.*[17,18] for reorientation development driven by surface free-energy minimization constraints under isothermal conditions and thus allows for a comparison between ion-assisted and non-ion-assisted behaviors. Finally, a comparison is made between the present models and existing theories and with experimental results, and suggestions are made for future studies.

II. GRAIN GROWTH AND ION IRRADIATION EFFECTS

A. Grain growth in a driving field

The theory of grain growth in a driving field is well established[53–55] and requires only brief reiteration here. The linear rate of grain expansion or grain growth velocity in one dimension can be written as

$$\frac{dL}{dt} = -M_G \frac{\partial \mu}{\partial x}, \tag{1}$$

where M_G is defined as the grain boundary mobility, and the driving force is the chemical potential gradient $\partial\mu/\partial x$. When grain growth occurs as a result of atomic defect migration across its boundary with its surroundings and there is a small chemical potential difference $\Delta\mu$ between these regions, then, at constant temperature T, there is a difference in the species jump rates across the boundary which leads to a grain boundary velocity

$$\frac{dL}{dt} = -c\nu_0\delta\frac{1}{kT}\exp\left(-\frac{Q}{kT}\right)\Delta\mu, \tag{2}$$

where c is a geometric factor depending upon the atomic mechanism, ν_0 is an effective local-mode frequency, δ is the local distance moved by the boundary per atomic rearrangement across the boundary, and Q is the mean activation energy for atomic jumps from either side of the boundary to the transition state at the boundary.

Knuyt *et al.*[17,18] used this equation with $\Delta\mu$ given by the difference between the surface free-energy density of a grain and the mean surface free-energy density of surrounding grains in their analysis of isothermal grain reorientation. Alexander and Was[48] modified the terms multiplying the chemical potential difference in a manner that will be explored subsequently for the case of thermal-spike-induced boundary motion, and in which this chemical potential difference was related to the interfacial free-energy density at the grain boundary, i.e., $\Delta\mu = -2\gamma/R$, where γ is the interfacial free-energy density and R is the grain radius. Processes driven by free-energy density differences between neighboring grains are classified as primary recrystallization while those driven by interfacial free-energy density are classified as secondary recrystallization, and since in the present study much of the interest lies in the mutual interaction between the bulk of neighboring grains to effect grain reorientation it is the former mechanism that will be employed. However, it will be necessary to modify the Knuyt *et al.*[17,18] approach to accommodate the transient thermal-spike-driven nature of the atomic migration events.

B. Ion irradiation effects

Extensive reviews of ion-irradiation-induced processes in materials already exist[56,57] and it is only necessary here to give a brief synopsis of those effects relevant to the present study. When an energetic ion approaches a surface it experiences repulsive forces from atoms of the solid, and if the ion energy is sufficiently low (usually in the tens of eV region) it will not penetrate beyond the first atomic layer but will be reflected. Estimates of the ion energy required to first effect penetration and the behavior of the penetration probability above this energy threshold have been made for ions incident onto random atomic arrays[58] and when ions are incident parallel to open (channeling) directions in crystalline substrates,[59–61] and in the latter case a major analysis of the channeling process in general was first given by Lindhard.[61] Quite expectedly, penetration is easier and its onset occurs at lower energies for channeled ions, and penetration is easier for heavy ions onto light substrates than the reverse situation. Even though at very low energies ions will not penetrate the surface, energy will be transferred to one or two surface atoms local to the point of impact and this energy will then be dissipated by phonon transport. This effect constitutes a thermal spike centered on the surface, and an effective temperature wave spreads out from the energy source. To the author's knowledge no estimates have been made of the behavior of this local energy deposition as a function of ion parameters (atomic mass, energy, and incident condition) nor of substrate parameters (atomic mass, crystallographic orientation, and, albeit weakly, temperature). Intuitively it would be expected that the fraction of incident ion energy deposited in this point spike would increase with ion energy and the ratio of the ion to substrate atomic masses. In this energy regime it is likely that few if any defects would be produced below the substrate surface.

As ion energy is increased to above the order of hundreds of eV and penetration occurs readily, an ion will be slowed down by a sequence of collisions with substrate atoms and will eventually stop in the bulk. The distribution of stopping positions will be statistical because of the randomness of initial and subsequent collisions with substrate atoms, and the mean and higher moments of the stopping distribution will increase with ion energy. For ion incidence close to channeling directions, a fraction of the ions will penetrate more deeply than in the case of random incidence. At each ion-atom collision energy will be transferred to the atom, and if this exceeds a displacement energy threshold the atom may be displaced from its lattice position. Indeed, if the energy transfer is large this primary atomic recoil may produce secondary displacement recoils and higher-generation recoils, and a displacement cascade of moving recoils ensues. This creates a vacancy population but a fraction of the equal number of interstitials produced may recombine with the vacancies. For light ions the cascade of defects will be dilute but for heavy ions, particularly in combination with heavy target atoms, the cascade will be dense and at the end of the ballistic collisional phase between atoms may resemble a vacancy-rich core surrounded by a mantle of surviving interstitials. The relaxation of the defect distributions will be by both thermal and athermal processes and will depend upon both the initial profile of the energy deposition function and the nature of the substrate material. This may involve survival of simple defects, production of extended defects, and phase change of the substrate, e.g., from crystalline to amorphous. In the present analysis it will be assumed, for simplicity, that the surviving defects are vacancies and interstitials only.

In the case of ion incidence close to channeling directions a fraction of the incident flux will be prevented from having close, displacement-generating, collisions near the surface and so the number of displaced atoms and resulting defects will be reduced. For a given substrate material the fraction of ions that were incident parallel to channeling directions and then become channeled increases with increasing ion energy and decreasing ion mass, and the defect production and survival densities follow the same behavior. Additionally, the channeling phenomenon is restricted to defined angular limits of the incident ion direction with respect to given channeling directions, and this angle increases with increasing ion and substrate atomic numbers and decreases with increasing ion energy and interatomic spacing along crystal rows parallel to channeling directions. Consequently, for ion incidence onto a system of randomly oriented polycrystalline grains, defect production will be minimized for those grains where their channeling directions lie within the critical channeling angle from the ion incidence direction, and this angle will follow the ion-mass and energy dependence just described. The channeling process, in minimizing energy transfer and deposition near the surface, also results in a reduction in the number of atoms sputter ejected from the surface.

Following the quenching of ballistic collisions between atoms these remain effectively ''hot'' and this energy is then redistributed both within the initial volume of the collision cascade and outside this volume. The effective initial temperature of the cascade volume will be proportional to the ratio of the ion energy deposited to the cascade volume and will be largest for heavy ions and substrate atoms. For ion energies not greatly in excess of those required for penetration, the initial thermal spike associated with this energy deposition may be regarded as of spherical geometry centered at a point just below the surface, but as ion energy is increased and penetration is deeper energy is lost more continuously along the ion path. In this case the thermal spike may be considered as of cylindrical geometry with a line source, in which the maximum initial temperature is given by the ratio of the energy deposition per unit length to the cross section of the cascade produced by the ion transverse to its path.

A significant difference between the spikes described here and that discussed earlier for nonpenetrating ions is that the former also occur together with defect production and it is the different influences that these spikes exert upon defect and surface atom migration and the resulting reorientation processes occurring between grains that will be analyzed in the following section. Initially, however, it is necessary to estimate more quantitatively how channeling processes may influence defect production and survival and, consequently, can modify the bulk free-energy densities of grains when these are growing continuously.

It is initially assumed that an energetic ion flux j_i is incident simultaneously with an atomic deposition flux j_a onto a crystal grain; the ions sputter the film growing onto the grain with a sputtering yield Y and penetrate the film and create $\eta(x)$ defects per unit depth of the film at a depth x beneath the instantaneous film surface. Both the ion and atomic fluxes are assumed to be incident normally to the substrate upon which deposition occurs. If the film grows with a velocity v in the $-Ox$ direction then at a time t after the start of deposition the defect production rate at a fixed plane parallel to and above the initial grain surface at a distance $-x'$ is given by $\eta(x'-vt)$. Consequently, as the film thickens, at this fixed plane the defect production rate varies and eventually a steady state is reached after the film has thickened to greater than the maximum depth of defect production, X, so that the defect density is proportional, at any depth from the surface except the portion of the film within the depth X from the initial grain surface, to the depth integral of the depth production rate function, i.e., to the total defect production rate $\eta=\int_0^X dx\, \eta(x)$. In fact, it is readily shown by analogy with the saturating collection of implanted ion species[62,63] that the equilibrium fractional defect concentration over the majority of the film thickness is given by $n=\eta j_i s/Nv$, where N is the atomic density of the film and s is the depth-independent probability for defects to survive annealing.

This model therefore assumes that, after production, defects may migrate and mutually annihilate or escape to sinks such as the free surface, grain boundaries, and dislocations. This happens on a time scale much faster than the time to grow a new surface layer and, after these processes are complete, only a fraction s of the defects survive and are stable. The saturation of defect density at any depth below the instantaneous surface then occurs when that depth exceeds the maximum range over which defects are produced. In a more exact analysis it would be necessary to solve the equations describing defect production, migration, and loss processes in a moving boundary (the surface) system, which, although can be accomplished readily for a stationary boundary,[64] has not, to the author's knowledge, been undertaken for a moving boundary. Consequently, in the present simplification, the survival probability s has been employed as an averaging parameter, but it would be expected, from analogy with the static boundary system, that s would be a function of such parameters as ion and atom flux densities, ion energy and species, and system temperature.

The rate of film growth is given by $v=(j_a-j_iY)N^{-1}$ if it is assumed that all arriving atoms condense on the film, and so the equilibrium fractional defect concentration is given by

$$n=\frac{\eta j_i s}{j_a-j_iY}. \tag{3}$$

If only point defect production is considered then η may be estimated from the Kinchin-Pease[65] equation as modified by Sigmund,[66]

$$\eta=\frac{0.42\, f(E_0)}{E_d}, \tag{4}$$

where $f(E_0)$ is the fraction of the incident ion energy E_0 deposited in elastic collision processes and E_d is the energy required to effect a permanent atomic displacement. More generally, the rate of defect production at depth x is given by

$$\eta(x)=\frac{0.42}{E_d}\,\frac{\partial f(E)}{\partial x}, \tag{5}$$

where $\partial f(E)/\partial x=F_D$ is the linear rate of elastic energy deposition.

Although Eqs. (3)–(5) are generally valid, when ion channeling occurs both the defect production rate and the sputtering yield will be reduced, since the elastic energy deposition densities in the bulk and at the surface will be reduced. As very simple linear approximations these processes can be written, in the presence of channeling with a probability p, as $\eta=\eta_0(1-p)/(1-p_0)$ and $Y=Y_0(1-p)/(1-p_0)$, where η_0 is the defect production rate for perfectly channeled ion incidence with a probability $p_0<1$ and Y_0 is the sputtering yield for perfectly channeled ion incidence. These linear forms should be regarded only as useful approximations that allow for facility of analysis. In fact, from studies by Oen and Robinson,[67] who assumed hard-sphere atomic collisions, it may be deduced that a power-law relation of the form $\eta=\eta_0(1-2p)/(1-2p_0)$ is a more exact description. For $p=p_0$ (perfect channeling) this leads to the same result as above while, for $p=0$ (no channeling) the defect production rate is larger than for any channeling conditions in both treatments.

Under atomic deposition and film growth conditions the geometric forms of each nucleus from which grains develop are expected to be identical, although their crystallographic orientations on the substrate can be variable, and so the normals to the surfaces of each grain will possess different angles with respect to ion flux direction and the channeling probabilities p for different grains will be different. Since the ion flux will be incident upon different surface crystallographic planes for different grains, the preceding linear approximation for the defect production rate will remain valid, but that for the sputtering yield will be slightly in error since this parameter is also dictated by the surface binding energy of atoms, which will depend on the surface crystallography. This perturbation will be ignored in the present analysis and the linear approximations for both rates will be substituted into Eqs. (3)–(5) to account for the channeling process.

The bulk free-energy density of a crystal containing a fractional defect concentration n is given by[53,54] $\mu=G+gn$, where G is the bulk free-energy density of a perfect, defect-free crystal and g is the additional free energy per unit fractional defect concentration. From studies by Wilkes, Liou, and Lott[68] of the similar problem of radiation-induced phase instability, this free energy will be equivalent to the enthalpy of point defect (e.g., vacancy) production, and this may be of the order of an eV or so. From the above discussion the bulk free-energy density difference between neighboring grains upon which ions are incident in different directions with respect to their major channeling directions, so that their respective channeling probabilities are p_1 and p_2, is thus given by

$$\Delta\mu = gs\eta_0 j_i\left[\frac{(1-p_1)}{j_a(1-p_0)-j_iY_0(1-p_1)} - \frac{(1-p_2)}{j_a(1-p_0)-j_iY_0(1-p_2)}\right]. \tag{6}$$

In the specific case where for two neighboring grains the ion flux is perfectly channeled for one grain and $p_1 = p_0$, while for the other grain the ion flux is completely unchanneled (random incidence) and $p_2 = 0$, Eq. (6) simplifies to

$$\Delta\mu = \frac{gs\eta_0 r}{(1-p_0)}\left[\frac{(1-p_0)}{(1-rY_0)} - \frac{1}{1-rY_0(1-p_0)^{-1}}\right], \tag{7}$$

where $r = j_i/j_a$, the ion:atom arrival rate ratio.

In Eqs. (6) and (7) both denominators in the bracketed term must be positive to ensure net film growth rather than sputtering-dominated erosion, and if growth is rapid and deposition is much greater than simultaneous erosion Eq. (7) can be further simplified to

$$\Delta\mu \approx -\frac{gs\eta_0 r}{(1-p_0)}\left[p_0 + \frac{rY_0 p_0(2-p_0)}{(1-p_0)}\right]. \tag{8}$$

It is already clear that the intergranular bulk free-energy density difference in the ion-assisted deposition case is a nonlinear function of the ion-to-atom arrival rate ratio, although for relatively small values of this ratio and/or small values of the sputtering yield the deviation from linear dependence will be weak. It is also clear that the bulk free-energy density difference is negative and increases with increasing channeling probability, i.e., the free-energy density of the grain for which channeling is optimum is lower than that for the grain for which channeling is absent, which indicates that the former will tend to grow into the latter in order to reduce the system free-energy density. This was the behavior suggested qualitatively by Van Wyk and Smith[27] and Dong and Srolovitz.[51]

III. THE INFLUENCE OF THERMAL SPIKES ON ATOM AND DEFECT JUMP RATES

When the ballistic collisional phase of atomic interactions has quenched and the deposited energy has equilibrated throughout the initial volume of the cascade, a thermal wave spreads out from this initial energy or equivalent ‘‘temperature’’ profile and the subsequent temperature profile is determined by the equation of heat conduction in an isotropic, uniform medium with thermal conductivity κ and heat capacity per unit volume C:

$$\nabla\kappa\nabla T = C\frac{\partial T}{\partial t}, \tag{9}$$

where both the thermal conductivity and the heat capacity may be constant or temperature dependent.

This equation has been solved, for constant values of these thermal parameters, exactly[69] and in a useful approximation;[70] and for conditions where the ratio of the thermal conductivity to the heat capacity (the thermal diffusivity) was assumed to be a simple power-law function of temperature[71,72] or where both parameters were assumed to be independent and different power-law functions of temperature. The rate per atom or defect at which a thermally activated process occurs is given by $\nu_0\exp(-Q/kT)$. Consequently, in order to determine the equivalent to the factor $P_T \equiv [\nu_0\exp(-Q/kT)]/kT$ of Eq. (2) when thermal spikes promote the reaction, it is first necessary to determine the temperature profile $T(r,t)$ as a function of spatial coordinates r and time t, then use this local and instantaneous value to determine the local and instantaneous reaction rate per atom or defect, and finally integrate this rate over appropriate space and all time. Division of this integrated rate by the total number of participant atoms or defects yields the desired factor. This type of calculation has been made for processes not driven by chemical potential differences for temperature-independent thermal conductivity and heat capacity,[70] and for thermal diffusivity assumed to be a power-law function of temperature,[71,72] for both spherical- and cylindrical-geometry heat conduction. It has also been made for the closely related problem of sputtering resulting from thermal spikes for both spherical- and cylindrical-geometry spike conditions and where the thermal conductivity and heat capacity were assumed to be independent power-law functions of temperature,[73–77] and for grain-boundary-curvature-related interfacial free-energy-driven processes for the case of cylindrical spikes.

In the case of thermal-spike-induced sputtering, it is the profile of the temperature wave across the surface that is relevant, as it is in the present study for the case of nonpenetrating ions that can mediate surface atomic migration. In the case of ions that just penetrate the surface, a point source spike in an infinite medium is considered since, on the one hand, the dependence on the system parameters of the form of the temperature profile is not modified by the initial position of the source but only its magnitude,[75–77] while, on the other hand, it is difficult to include the effects of a boundary in the case of temperature-dependent thermal constants.[73–77] In this case also the reaction participants are considered, in the present work, to be the equilibrium density of surviving defects contained within the depth X from the film surface. For higher-energy, more deeply penetrating ions, cylindrical spike geometry and the surviving defect population throughout the entire film thickness are employed.

In the present analysis similar calculations have been performed for temperature-dependent thermal constants but, as in the previous studies indicated above, the variation of the factor P with the system parameters is weak and only the magnitudes are slightly changed, and so the results for temperature-independent values only are quoted here.

For the case of low-energy, nonpenetrating ions which deposit an energy E_0^* in a point spike at the surface and from which a hemispherical thermal wave then spreads,

$$P_{\mathrm{HS}}=\frac{K_1 j_i \nu_0 (kE_0^*)^{4/3}}{\kappa C^{1/3} Q^{7/3}}. \tag{10a}$$

For the case of low-energy, penetrating ions which deposit an energy E_0 in a point spike just below the surface and from which a spherical thermal wave then spreads,

$$P_{\mathrm{SB}}=\frac{K_2 j_i \nu_0 k E_0^{5/3}}{\kappa C^{2/3} Q^{8/3} X}. \tag{10b}$$

For the case of higher-energy, penetrating ions which deposit energy continuously throughout a film thickness at a linear rate F_D in a line spike and from which a cylindrical thermal wave then spreads,

$$P_{\mathrm{CB}}=\frac{K_3 j_i F_D^2}{\kappa C Q^3}. \tag{10c}$$

In these equations the constants K are calculable and are related to the geometry and the spatial integration and are all in the region 10^{-3}–10^{-2}. It may be noted that in these equations a common value of the activation energy Q has been employed but it is entirely possible that such values will differ according to whether the process is one of surface atomic migration or bulk defect migration.

As an illustration of the probable importance of thermal spike effects a system is considered at 300 K for which an activation energy $Q=1$ eV is chosen and a local-mode frequency $\nu_0=10^{13}$ is assumed, together with generic order-of-magnitude values for metals of $\kappa=10^{21}\,\mathrm{eV\,m^{-1}\,K^{-1}\,sec^{-1}}$ and $C=10^{25}\,\mathrm{eV\,m^{-3}\,K^{-1}}$ and a typical ion flux density of $1\,\mathrm{mA\,cm^{-2}}\approx 6\times 10^{19}\,\mathrm{ions\,m^{-2}\,sec^{-1}}$. Appropriate values of E_0^*, E_0, X, and F_D for the three spike geometries discussed above may be assumed to be of the order of 10 eV, 1 keV, 1 nm, and $1\,\mathrm{keV\,nm^{-1}}$, respectively. For these assumed values the magnitudes of P_T, P_{HS}, P_{SB}, and P_{CB} are 4×10^{-3}, 2×10^{-4}, 2×10^{-1}, and 5×10^{-1} (all in units of $\mathrm{jumps\,sec^{-1}\,eV^{-1}}$) respectively, when lower values of the constants K are used. It may be remarked that the similarity in the magnitudes of the final two values above arises rather naturally, since the ratio of the initial ion energy to the depth over which equilibrium defect concentrations are established for the lower-energy ion case is the same as the linear rate of energy deposition density for the higher-energy ion case.

Clearly, all of the spike-induced processes can be of similar or larger magnitude than isothermal processes for a specific driving force mechanism, and in the case of low-energy, nonpenetrating ions in particular the spike process can dominate the thermal mechanism if the ion flux density and/or the ion energy deposited and/or the activation energy for surface atomic migration is increased or the system temperature is decreased. In fact, because of the largely exponential dependence on these latter two parameters it is these whose magnitudes largely condition the dominance of isothermal or spike effects. Equalization of P_T and P_{HS} leads to an approximate value of the temperature T_c at which these two processes become of equal importance, given by

$$T_c=\frac{Q}{k}\,\frac{1}{\ln \kappa C^{1/3}(K_1 j_i)^{-l}(kE_0^* Q^{-1})^{4/3}}. \tag{11}$$

This relation clearly indicates the dominant role of the surface migration energy in determining the temperature at which spike processes will become dominant, and the much weaker dependence of this temperature on ion flux density and the deposited energy per ion. For the values of the system parameters given above, this critical temperature is evaluated to be approximately 285 K, which implies that, for the system parameters assumed, which are typical of many ion-assisted deposition situations and material constants, the effects of thermal spike processes, even with very low-energy ions, will be observable near room temperature.

It should be reiterated that the role of thermal spikes in this ion energy regime is to supplement any isothermal processes drives by free-energy density differences, so that any such process that tends to minimize total surface free energy will be accelerated by the operation of thermal spikes. On the other hand, as ion energy is increased and penetration and defect production occur, then the channeling effect will begin to assume importance. The system will then tend to be driven toward a state of minimum volume free-energy density with major crystallographic channeling directions aligned parallel to the incident ion flux direction. For fcc materials this will tend to orient crystal grains with their surfaces parallel to {110} planes, while for non-ion-assisted and for low-ion-energy-assisted deposition grain surfaces will tend to be oriented parallel to {111} planes.

In this higher-energy ion regime it is clear, from earlier comparisons of P values, that for any given driving process thermal spikes are likely to be even more dominant than purely isothermal effects. Equations (10a)–(10c) reveal the variations in P values as, for example, ion energy is increased, but the energy at which any transition from thermal spike effects supplementing isothermal processes to minimize surface free-energy density to thermal spike effects and simultaneous bulk defect production, which compete with surface processes and tend to minimize volume free-energy density, cannot be deduced from simple comparisons of P_{HS} and P_{SB}, since the driving free-energy difference will be different in the two cases. It is therefore necessary, in the next section, to evaluate the free-energy difference between grains when channeling becomes important for penetrating ions, using the results obtained from Sec. II, and hence to obtain estimates of grain growth rates. Initially this is done for a simple system of two neighboring grains which possess maximum channeling and zero channeling fractions, respectively. These results are then employed in the subsequent section to evaluate the rates at which grain reorientation occurs for systems in which either surface or volume free-energy minimization is the driving mechanism.

Finally, it may be noted that the influence of the substrate material can be further refined by assuming, following Alexander and Was,[48] that the process activation energy Q and the cohesive energy of the film material ΔH_{coh} are linearly related and substitution of this relation into Eqs. (10a)–(10c).

IV. THE INFLUENCE OF THERMAL SPIKES ON GRAIN GROWTH RATES

The volume free-energy difference between grains in which the optimum and zero channeling occur was derived in Eq. (8), and it is useful, initially, to compare this value with that employed by Alexander and Was,[48] who estimated the grain growth rate when cylindrical-geometry thermal spikes accelerated this rate under the driving influence of interfacial free energy between a grain and its surroundings. From the values $\gamma = 3\times 10^{18}\,\mathrm{eV\,m^{-2}}$, $\Omega = 15\times 10^{-30}\,\mathrm{m^3}$, and a typical grain radius $R \approx 10^{-8}$ m used by these authors, a value of the interfacial free energy of the order of 0.05 eV per atom was deduced. If, in Eqs. (4) and (8), a value of the ion:atom arrival rate ratio of unity and a typical value of $E_d = 25$ eV, are chosen together with a value of the initial ion energy E_0 of 10 keV (which is a reasonable order of magnitude to be able to assume sufficiently deep ion penetration and to describe the spike as linear rather than of point geometry), and if the effects of simultaneous sputtering erosion are neglected in a first-order approximation [again, this is reasonable since the term in Eq. (8) that describes this process contains the additional channeling fraction p_0], and if this fraction is, again reasonably for heavy ions, assigned a value of 0.1, then for values of the defect survival probability s ranging from 10^{-4} to 10^{-2} the free-energy difference $\Delta\mu$ between grains aligned so that channeling is optimum and those in which no channeling occurs ranges from 4×10^{-3} to 0.4 eV per atom. The values of the point defect survival probability are not well known and will certainly decrease with increasing system temperature as a result of thermally induced annihilation but, in addition, athermal annealing effects due to lattice strain associated with point defects will limit the maximum value of the fractional point defect concentration to the order of 10^{-2} in metals.[78] This indicates that a larger value of the defect survival probability chosen above will represent a maximum value of this quantity rather than it being constrained by the ratio of rates of defect production to film growth determined earlier. It is clear, however, that this free-energy density difference range encompasses the free energy associated with grain-boundary curvature (i.e., $\approx$0.05 eV atom^{-1}), and as grain size and radius increase the volumetric free-energy density differences may substantially exceed interfacial free energies. Since the factor P derived in Eq. (10c) and the parameter δ are essentially identical to those derived by Alexander and Was,[48] it is clear that the rate of grain growth resulting from ion irradiation may be equally as plausibly explained by the volume free-energy density differences arising from the differential channeling between grains as by that resulting from the interfacial free energy of grains. This former mechanism is that advocated by Van Wyck and Smith[27] and Dong and Srolovitz[51] and it is evident that the present estimates of volumetric free-energy differences and the enhanced defect jump rates resulting from thermal spike processes demonstrate the reality of this mechanism.

It is also worth noting that, in their analysis of thermally driven grain growth and reorientation, Knuyt *et al.*[17,18] use a value of the surface free-energy density difference between grains of the lowest and highest free-energy densities of the order of a fraction of an eV, i.e., of similar magnitude to that derived here for volumetric free-energy density differences.

Since the present analysis shows that the volumetric free-energy density differences resulting from differential channeling processes between grains are of similar magnitude to those that arise from other sources, it is legitimate to evaluate the rate of grain expansion for a bicrystal system in which the volumetric free-energy density difference is a maximum as considered above, and when thermal spike processes in the bulk accelerate defect jumps. This rate of expansion of the grain of lowest volumetric free-energy density into a neighbor grain of highest free-energy density may be calculated from the analog of Eq. (2) rewritten as

$$\frac{dR}{dt} = -P_S \delta \Delta\mu, \tag{12}$$

where, for simplification, c is assumed to be unity and P_S represents the P factor for either spherical or cylindrical spikes generated in the bulk. P_S can be evaluated from either Eq. (10b) or Eq. (10c). It is of similar magnitude for the system parameters assumed earlier and of the order of $10^{-1}\,\mathrm{sec^{-1}\,eV^{-1}}$ in both cases. δ will be of the order of a few tenths of a nanometer and if, from the earlier discussion, a volumetric free-energy density difference of $\Delta\mu \approx 0.1$ eV is assumed, the rate of grain expansion is of the order of $10^{-3}\,\mathrm{nm\,sec^{-1}}$. Although slow, apparently this rate is comparable to the film growth rate that would occur with a net deposition flux of atoms of the order of $10^{16}\,\mathrm{atoms\,m^{-2}\,sec^{-1}}$, which is somewhat small. In molecular dynamics studies of grain reorientation the pictorial evidence given by Dong and Srolovitz[51] of the occlusion of nonchanneling grains by channeling grains occurs at a rate substantially slower than the film growth rate, with which the above comparisons are not in disagreement.

Given this reasonable qualitative and order-of-magnitude agreement it is now justifiable, as in the next section, to evaluate the rates at which grains reorient toward those of maximum channeling probability from an initial random distribution of grain orientations. Before doing this, however, it is useful to return to an assessment of the criterion for which there is a transition between low-energy, nonpenetrating ion-irradiation-induced thermal spikes centered on the surface, which accelerate normal isothermal processes driven by surface free-energy density differences, and higher-energy, penetrating ions, which generate bulk defects and thermal spikes accelerating the grain reorientation process driven by volumeric free-energy density differences. In order to determine the ion energy at which this transition occurs, it is necessary to compare the values of P given in Eqs. (10a) and (10b) when each is multiplied by its appropriate free-energy density difference. As noted above, these free-energy density differences for both surface-driven and bulk-driven effects are likely to be of a similar magnitude, and so it is now acceptable to compare only Eqs. (10a) and (10b). When this is done and it is assumed that at the transition energy E_0^* and E_0 should be equal, it is readily shown that the transition energy is given by

$$E_{0T} \approx \frac{CQX^3}{k}. \tag{13}$$

For the values of the parameters $Q = 1$ eV and $X \approx 1$ nm assumed earlier, this leads to a transition energy of the order of 100 eV, which is clearly particularly sensitive to the assumed value of X. It is difficult to prescribe this distance accurately, since if the ion energy is just sufficient to allow penetration and defect production the defects will be produced close to the surface and image forces may result in their loss to the surface, thereby reducing the additional volumetric free-energy density difference as well as modifying the P factor. Nevertheless, it is reasonable to conclude that this energy will probably lie between tens of eV at which ion penetration becomes possible and 100 eV or so when stable bulk defect production is feasible.

V. THE RATE OF GRAIN REORIENTATION

As indicated earlier this phase of the analysis is based upon previous investigations by Knuyt *et al.*,[17,18] who determined the rate at which grains of minimum surface free-energy density grew into a surrounding grain population of higher surface free-energy densities and in which the initial population of the grains was uniformly and randomly distributed. It is therefore helpful to summarize the approach and results of these authors in order to apply the approach to the present model proposals. Knuyt *et al.*[17,18] assumed that a growing film was composed of cylindrical columns with common crystallographic structure and with their planar interfaces with the external environment. The columns, however, were differently oriented with respect to the normal to the mean surface and the initial substrate. Consequently, the surface free-energy densities of individual columns were different, and it was argued that the columns with lower surface free-energy densities would expand into surrounding columns if the mean surface free-energy density of the immediately surrounding columns was higher. An initial population of uniform columns of radius R_0 was assumed, in which the normals to each columnar surface were randomly distributed in polar angle with respect to the normal to a surface of minimum free-energy density. These authors also assumed a specific form for the variation of the surface free-energy density with polar angle ϕ with respect to the surface of minimum free-energy density, although their analysis was also undertaken for a general relationship of this function. At a given time t during deposition a modified form of Eq. (2) was employed, in which the free-energy density difference $\Delta\mu$ was replaced, as indicated above, by the difference between the surface free energy of a specific grain i and the mean surface free-energy density of its immediately surrounding grains, i.e.,

$$\frac{dR_i}{dt} = -\frac{\nu_0 \delta}{kT}\exp\left(-\frac{Q}{kT}\right)(\Gamma_i - \Gamma_m), \tag{14}$$

where Γ_m was determined from the relation $\Gamma_m = \Sigma_j \Gamma_i M_i R_i / \Sigma_j M_j R_j$, in which M_i is the number density of i columns. Equation (14) was solved by both computational simulation and approximate analytical methods for both short and long deposition times with good agreement between the two approaches. For short times, where it may be assumed that columns of all orientations are still present in the total population, the analysis can be extended to show that

$$\frac{dR_i}{dt} \approx P_T \delta(\Gamma_0^* - \Gamma_i), \tag{15}$$

where $\Gamma_0^* = \omega_1/\omega_0$ and the ω values are defined from the generalized moments $\omega_n = \int_0^{\phi_{\max}} \Gamma(\phi)^n \sin\phi\, d\phi$, where $\phi_{\max}$ is the maximum angle in the surviving angular range of columnar surface orientations at time t. This attrition of the angular range occurs because the columns of lower surface energy density expand at the expense of columns of higher free-energy density and so the latter are gradually occluded from the depositing atomic flux. For small times the upper limit of the above integral may still be assumed to be the $\pi/2$ of the initial random orientational distribution, and the maximum rate of initial grain growth is obtained for grains with the minimum surface free-energy density Γ_0 growing into the surrounding random orientational columnar structure. For their assumed functional dependence of $\Gamma(\phi)$ for the specific case of growth of TiN grains, $\Gamma_0^* \approx 1.275\Gamma_0$. It may be assumed that for many systems the difference between the lowest and the mean surface free-energy density planes is a similarly small fraction e of the minimum surface free-energy density plane, and so in general the maximum rate of initial grain growth from an initially randomly oriented population of grains can be written as

$$\frac{dR_{\max}}{dt} \approx P\,\delta e \Gamma_0. \tag{16}$$

This equation has been written in generalized form with the factor P since it is not only applicable to the isothermal grain growth process discussed by Knuyt *et al.*,[17,18] but is equally relevant when grain growth is influenced by the thermal spike mechanisms under examination in the present work.

The above approach can be directly carried over into the present study by replacing the driving process for grain reorientation of differences in surface free-energy density with differences in volumetric free-energy density resulting from differential ion channeling effects between differently oriented grains. Additionally, it is necessary to suitably modify the effective variation of grain free-energy density as a function of grain orientation to account for the channeling process. In the work of Knuyt *et al.*,[17,18] it was possible to describe the surface free-energy density as a continuous function of the orientation of grain surfaces with respect to the surface plane of minimum free-energy density. In the case of ion-assisted deposition, where channeling processes modify the volumetric defect densities of grains and, as a result, their volumetric free-energy densities, channeling is confined to a restricted angular range $0<\phi<\phi_c$ with respect to the direction of maximum channeling, and outside this range, $\phi_c<\phi<\pi/2$, channeling may be assumed to be absent.

Consequently, in an initially random population of grain orientations, that part of the population with angular orientations within the channeling angular range will develop a singular, common volumetric free-energy density, and that part of the initial distribution outside the critical angular range will develop a different common, angle-independent and higher volumetric free-energy density, i.e., the free-energy density function will be discontinuous at $\phi=\phi_c$. It is straightforward to substitute this free-energy density variation function into the definition of the free-energy density moments of Knuyt *et al.*[17,18] We recall that, within the critical angular range for channeling, the channeled fraction is p_0 and it is zero elsewhere. Then we evaluate the maximum initial grain growth rate for this system. The final result is

$$\frac{dR_{S\,\max}}{dt} = -P_S \delta \cos \phi_c \Delta \mu \tag{17}$$

where $dR_{S\,\max}/dt$ is the maximum initial grain growth rate, P_S is the P factor appropriate to either spherical or cylindrical geometry spikes in the bulk given by Eqs. (10a) or (10b), and the relevant free-energy density difference $\Delta\mu$ is given by Eq. (8). Since the critical angle for channeling is usually small, the cosine factor in Eq. (17) can safely be approximated as unity. The presence of this term results from the fact that, as the critical angle increases, a larger fraction of grains will be initially oriented within the critical angular range, and any one grain in this range will be surrounded by a higher fraction of grains also falling in this range, so that the average driving free-energy density difference will be smaller and the grain growth rate will be lower.

Clearly Eq. (17) can be written in its full, cumbersome detail by insertion of these appropriate relations for spikes of both spherical and cylindrical initial geometry, but, although giving completeness of analysis, it is unnecessary in view of the earlier discussions of the magnitudes of the different P factors corresponding to isothermal, surface spike, and bulk spike conditions, and of the magnitude of the volumetric free-energy density difference resulting from the channeling effect in comparison with surface free-energy density differences between grains of different surface planar geometry and interfacial free-energy density. In the latter case in particular it has been demonstrated that, for reasonable choices of system parameters, which correspond to achievable experimental conditions such as the ion to atom arrival rate ratio, the incident ion energy, the channeled fraction, and the point defect survival probability, these free-energy density differences can be of similar magnitude. Consequently, and independent of any influence of thermal spike phenomena, intergranular volumetric free-energy differences arising from differential channeling can be at least as significant as these other driving influences and potentially more important, and could either supplement or compete with such processes in causing grain reorientation. For low-energy, nonpenetrating ions, where bulk defect production is absent, no such mechanism will exist but, according to the evaluations of the factor P for purely isothermal grain growth and for surface thermal-spike-mediated growth, the latter mechanism will be dominant. This leads to enhanced growth rates of minimum surface free-energy density grains for sufficiently large incident ion flux densities and energy deposited per ion, and this enhanced rate will be determined by the value of P_{HS} in Eq. (10a). For higher-energy, penetrating ions, evaluations of the magnitudes of P_S for either spherical or cylindrical spikes generated in the bulk showed these to be generally similar, and to be substantially greater than P values for either isothermal (at room temperature for the surface atomic migration energy assumed) or surface-centered thermal spikes. Therefore for such ion irradiation conditions the channeling effect that led to differences in defect densities between grains becomes the dominant process, and the system tends to develop toward one in which all grains are oriented so that their major channeling directions are parallel to the incident ion flux direction. In this case Eq. (17), with values of the system parameters used in Sec. IV, indicates that the maximum initial growth rate for grains oriented within critical acceptance angle for channeling is as deduced in that earlier discussion.

Next it may be noted that, using the above type of analysis, an approximate estimate can be made of the time required, from an initial random distribution of grain orientations, for all of those grains that were initially oriented within the critical channeling angular range to have expanded and occluded all other initially oriented grains. The result in a linear first-order approximation is

$$t_{\mathrm{occ}} \approx \frac{R_0}{P\delta \cos \phi_c \Delta\mu}, \tag{18}$$

although in higher-order approximations the occlusion process is more gradual and tends to occur as a quasiexponential decay effect. This equation does illustrate, however, that the greater the role of thermal-spike-mediated defect migration between grains of maximum and zero channeling, the more rapid will be the tendency toward grain reorientation close to channeling incidence conditions. The earlier discussions indicate that this will be best achieved for large values of incident ion flux density and ion-to-deposit-atom arrival rate ratio, provided that the congruent sputtering erosion does not prevent net film growth, high-energy deposition densities per ion so that the effective initial temperatures of spikes are high, and large values of the channeled fraction and the defect survival probability.

Finally, it may be noted that Knuyt *et al.*[16,17] also derived an expression for the surviving grain density, defined as the fractional surface area of all columns with orientations between ϕ and $\phi + d\phi$ per unit solid angle in this range. The density is given by $D(\phi,t)$ and is proportional to $\pi R_i^2 M_i / M_i$ since, initially for a randomly oriented grain distribution, M_i is proportional to the solid angle in this range. Extending the analysis of Knuyt *et al.* to the present approach leads to the result, applicable for small times t and for grains oriented outside the critical angular range for channeling,

$$1 - \left(\frac{D(\phi,t)}{D(\phi=0,t)} \right)^{1/2} \approx \Delta\mu \frac{P\delta t}{R_0 + P\delta\Delta\mu \cos \phi_c t}. \tag{19}$$

For larger times the denominator on the right-hand side of this equation becomes a power-law series in time with only additional terms of even index in time and odd index of the powers of the product $P\delta$, which are all negative. Consequently, the fractional surface area of grains that are oriented outside the critical channeling angle is, as expected, a decreasing function of time, and the larger the factor P the more rapidly will this fraction decrease. This rate of decrease will also be larger the greater is the free-energy density difference between grains for which channeling is a maximum and zero.

VI. DISCUSSION

The preceding discussion has demonstrated analytically, and by making order-of-magnitude estimates, that differences in volumetric free-energy density between grains for which there are different ion channeling probabilities, and consequently different surviving point defect densities, can be similar to both surface free-energy density differences and interfacial free-energy densities, and so can be, at least partly, responsible for grain growth and reorientation phenomena in ion-assisted deposition. Furthermore, the thermal spikes that follow the collisional stage of ion impacts can induce at least as many, if not far more, activated atomic or defect jumps than can purely isothermal processes alone, and can either enhance the surface atomic migration rate and lead to more rapid tendency toward minimization of surface free-energy density (for nonpenetrating low-energy ions) or compete with this mechanism (for penetrating, higher-energy ions) and lead toward a granular structure in which volumetric free-energy density is minimized and the channeling process is optimized. It is now useful to examine, in somewhat more detail, the system parameters that favor one or the other process.

First the basic assumptions of initial spike geometry are considered. In the derivation of Eqs. (10a)–(10c), either a point spike in which ion energy was deposited instantaneously or a line spike along which energy was deposited instantaneously defined the initial geometry as in a number of previous studies.[48,70–74] As indicated earlier, at the end of the collisional stage following ion impact, energy will be equilibrated throughout the volume of the collision cascade, and an effective maximum temperature of atoms in this volume can be assigned. This can form a different initial condition from the point or line geometry defined above. If the cascade volume is small and/or the deposited energy is large, these two conditions are very similar, but if these requirements are not met the initial conditions, and the magnitudes of the resulting temperature profiles and consequent jump rates, may differ substantially. Sigmund and Claussen[75] and Claussen[76,77] showed, for cylindrical and spherical spike geometries, that jump rates declined almost exponentially with the reciprocal of the deposited energy density. This can be calculated analytically[79,80] and, after a small initial decrease for low-energy ions, increases with ion energy and with increasing film atom-to-ion mass ratio. Consequently, for light ions incident onto heavy-atomic-mass films the average initial effective temperatures in cascade volumes will be low, and the point or line spike models may considerably overestimate jump rates, whereas for heavy ions the approximations will be more acceptable. The preceding analysis is, therefore, best suited to experimental conditions of the latter type.

Considering next the values of the activation energy Q employed in the calculations of atomic or defect jump rates, it was already noted that these may differ according to the process involved. Since the molecular dynamics studies[50,51] have not explicitly identified the nature of the migrating point defect species responsible for grain growth and reorientation processes to minimize volume free-energy density, it is not possible to predict an appropriate value for the species activation energy for this mechanism. In general, however, in metals the migration energy for interstitials is much lower than that for vacancies, and the former may therefore migrate more rapidly to fixed sinks such as nearby surfaces and indeed the grain boundaries to effect the recrystallization process. On the other hand, during deposition, the migrating surface species will largely be deposited adatoms for which energies of formation will not be required, unlike atoms located in the first filled surface atomic plane, and the migration energies of these adatoms may not be too different from bulk interstitial migration energies. Furthermore, some experimental evidence[81,82] indicates that even low-energy, penetrating ions generate interstitials, which escape vacancy capture, migrate to the surface, and become additional adatoms. If, therefore, surface adatoms and bulk interstitials are the species responsible for the differing grain growth processes, the values of the activation energies for these processes may be quite similar and the earlier comparisons of jump rates will remain appropriate.

Estimates were made above of the ion energy at which the transition from supplementing surface migration to producing bulk defect diffusion occurred, based on the premise that such defects survived even when generated close to the surface. As just indicated, thermal migration may denude the near-surface region of defects, while a thermal image forces may further contribute to this denudation. Consequently, the promotion of surface atomic migration may continue to ions of higher energy than suggested earlier and the estimate of the transition energy should be regarded as a lower limit.

Considering next the parameters that influence granular volumetric free-energy density differences in the ion channeling process, the two variables critical channeling angle and channeled fraction are of importance. For high-energy ions the critical channeling angle scales[61] as $\phi_c \propto (Z_1 Z_2/E_0)^{1/2}$, whereas for low energies the critical angle scales as the square root of this parameter, where Z_1 and Z_2 are the atomic masses of the ion and film atoms, respectively. Clearly, the critical angle is larger for heavier ions and film atoms and for low-energy ion incidence. The channeled fraction scales as $p_0 = 1 - A q_c^2$ where A is a constant dependent upon the crystal geometry and q_c^2 is the impact parameter between an ion and an atom at which scattering through the critical angle occurs. For low-energy ions the critical angle and impact parameter are approximately linearly related, and for a fixed value of the former the critical impact parameter scales as $q_c \propto \ln Z_1 Z_2[(M_1 + M_2)/M_2 E_0]$, where M_1 and M_2 are the atomic masses of ions and film atoms, respectively. For higher energies the critical angle and impact parameter are approximately hyperbolically related and for fixed critical angle this impact parameter scales linearly with the term in the logarithm above. Thus, overall, the channeled fraction will increase with increasing ion energy and decreasing ion mass for a given film material, as discussed qualitatively earlier. As a result of these two factors, when low-energy ion irradiation is used the fraction of grains initially oriented within the critical channeling angular range can be large but the fraction of ions that can be channeled when incident on such grains can be small, and there is a combined effect, which is also a function of ion energy, on the overall influence of channeling for a given film material, as is evident from Eqs. (17) and (18). It may also be remarked that the above expression for the channeled fraction is only approximate and does not account for the effect of increasing atomic thermal vibrations with increasing temperature. When this is accommodated the channeling fraction becomes a decreasing function of temperature.

A further important parameter in determining volume free-energy density differences is the point defect survival probability s. It has already been suggested that this will be composed of two parallel effects, an athermal mechanism with probability s_A and a thermal mechanism with probability s_T operating in parallel so that $s=s_A s_T/(s_A+s_T)$. The athermal mechanism will dominate at low temperatures but as temperature is increased thermal annealing of defects will become predominant. If it is assumed that this annealing process can be characterized by an activation energy Q^*, then at higher temperatures s is replaced in Eqs. (6)–(9) by $s_T = s_{T_0}\exp(-Q^*/kT)$. If the activation energies Q and Q^* are similar, this has the effect, in Eqs. (10a)–(10c), of reducing the P values by only approximately $1\rightarrow 2^{-m}$, where m is the relevant exponent of Q in these equations and is obviously a small perturbation. If, however, Q^* is much smaller than Q, the P values are reduced by a factor mQ^*/Q, which may be far more substantial and reflects the defect loss process. The consequence of this is that, as temperature is increased, not only will surface atomic migration proceed more rapidly but there will be a reducing influence of volumetric processes, and the tendency will be for the minimization of surface free-energy density mechanisms to dominate. If it were possible to assign known values to these activation energies, then similar estimates to that for the transition ion energy could be made for the process transition temperatures by comparison of the P factor in Eqs. (10a) with that of (10b) and (10c).

The above discussion is based upon the assumption that an average value of s, which accommodates the effects of rapid defect diffusion and loss, can be used to characterize the surviving point defect fraction that is saturated by the moving boundary (surface) process. As indicated earlier, this may be a considerable oversimplification, and the surviving point defect population will saturate when the processes of defect generation (which will be curtailed by the moving surface) and loss by recombination and to sinks are equal. This will inevitably lead to more complex dependencies of point defect densities, and resulting volume free-energy densities, on incident ion and atom parameters and system temperatures. In turn this will lead to more complex dependencies of grain growth rate on, for example, j_i and j_a than would be predicted through use of Eqs. (2), (8), and (12). Consequently, tests of model validity would be to experimentally measure single-grain growth rates as functions of both these fluxes and system temperature in order to establish if the present simplifications require revision. Even if the assumption of an average survival probability is approximately correct, important variables in determining the overall grain growth and reorientation are, to first order when simultaneous sputtering is neglected, not simply a function of the ion-to-depositing-atom arrival rate ratio r but are linear functions of $j_i^2/j_a \equiv j_i r$. when the sputtering process is included there is a higher-order correction term proportional to $j_i r^2$. It is also evident from these equations that grain growth and reorientation rates are not simple functions of the energy delivered to the film per depositing atom in the presence of ion irradiation $j_i E_0/j_a$ since the dependence on E_0 is a power-law function, the exponent of which increases slowly with increasing ion energy. The energy per deposited atom was suggested by Harper *et al.*[83] to be a useful parameter to describe various properties of deposited films although Petrov *et al.*[23] subsequently demonstrated that this single parameter was an inadequate descriptor and that film properties were better described in terms of independent functions of ion-to-deposited-atom arrival rate ratio and ion energy, in qualitative agreement with the present observations.

The present treatment of grain evolution assisted by thermal spikes that enhance defect jump rates between grains of different volume free-energy density was based on the assumption that equilibrium defect densities are established in grains during growth by surface recession. If, on the other hand, defect mobilities are so large that a fraction of these immediately escape to grain boundaries, rather than being driven by free-energy differences, and the remainder escape equally rapidly to other sinks such as the free surface, the number of additional atomic or defect jumps per deposited atom will scale linearly with r, and the jump frequency per ion will be given by P/j_i where the P factor will be given by the appropriate Eq. (10a)–(10c), but in which the indices of k and Q are reduced by unity because of the absence of the driving factor $\Delta\mu/kT$ relevant to the specific ion energy regime. In this case the effect of channeling will be to directly modify the defect production and equal loss rates to common grain boundaries where there are different channeling fractions. Although a linear dependence of grain growth on r can be recovered in this way, the nonlinear dependence on ion energy remains and neither current experimental results referred to in the Introduction[26–48] nor molecular dynamics simulations[50,51] are able, as yet, to distinguish which of the defect-related mechanisms is dominant.

Finally, in their analysis, Knuyt *et al.*[17,18] employed a common, initial column radius R_0 for the randomly oriented grain population, since their studies were concerned with growth onto a polycrystalline substrate. More generally, growth may be initiated onto amorphous materials on which randomly oriented grains first nucleate and then expand to produce a quasicolumnar structure, and it is only from this stage of evolution that the grain reorientation analysis becomes valid. The time, or effective deposited film thickness, at which this will occur increases as the equilibrium areal density of nuclei decreases, and this density is known to be affected by simultaneous ion bombardment[22,81,82,84–86] due to a variety of processes. These include irradiation-induced generation of additional nucleation centers,[81,82] dissociation of and modification to the surface diffusivity of nucleated islands,[84,85] and sputtering of surface adatoms and modification of their diffusivity.[86] It is not, as yet, easy to predict the variation of nuclei density with incident ion parameters such as energy and flux density, the depositing atom flux density, or film parameters such as material type and temperature. Consequently, at present it is only possible to observe, qualitatively, that an incubation time dependent on the system parameters is always likely to occur before grain reorientation processes will be observed, and this time should be subtracted from experimental observation times when equations such as (16)–(19) are employed for comparison with these measurements. Additionally, in order to make such comparisons, it will be necessary to measure the mean columnar radius R_0 at the onset of columnar growth.

Although the above discussion has only been semiquantitative because of imprecise knowledge of many of the relevant system parameters and processes, it still remains plausible that, particularly for heavy ions and substrate atoms and medium-energy ions in the 10–100 keV range where bulk thermal spikes will be produced and where channeling fractions will be significant, and for lower-energy ions where surface-centered spikes will operate, the present analysis gives order-of-magnitude estimates of the tendencies for grain reorientation toward optimized channeling conditions in the former case and a more rapid reorientation toward grains of minimum surface free-energy density in the latter. It is therefore useful to compare the present approach with both alternative models and experimental data although, as will become apparent, in neither case is there a substantial and comprehensive data base.

It has already been indicated that the present estimates of the role of cylindrical-geometry thermal spikes in promoting grain growth are essentially identical to those of Alexander and Was.[48] The essential difference in the determination of grain growth rates between the two approaches is the assumption of volumetric free-energy density differences between grains in the present case and interfacial free energy of curved grain boundaries in the work of Ref. 13. The magnitudes of the effective driving forces were shown to be similar and so it is possible that both effects may operate simultaneously. It should be recognized, however, that Alexander and Was implicitly assumed equal orientation of all grains so that, even in the absence of ion irradiation, there would be no tendency for the growth of low surface free-energy density grains at the expense of their surroundings. In the presence of ion irradiation the present treatment has demonstrated that for low-energy ions this surface free-energy minimization mechanism can be augmented, while for higher-energy ions volumetric free-energy density differences can also enhance grain growth rates but, importantly, the surface orientations of the grains will tend toward different planes in the two cases. Since common grain habit was assumed in their approach, the Alexander and Was mechanism alone cannot be employed to predict grain reorientation processes, only grain growth rates. However, their estimates of the influence of thermal spikes for higher-energy penetrating ions remain valid and can be used, as in the current analysis, to determine both grain growth and reorientation rates if the present, grain-orientation-dependent, volume free-energy density difference driving mechanism is employed. The same general approach is also valid for lower-energy ions but either spherical or hemispherical spike geometries should be used. It is interesting to observe that in Alexander and Was's model the grain growth rate is predicted to be linearly dependent upon grain curvature R^{-1}, whereas the present model, through Eqs. (8), (10), (16), and (17), predicts no dependence of growth and reorientation rates upon curvature. It may be observed that in the case of postdeposition irradiation there is no longer a simultaneous growth process and, in the present model approximation, point defect saturation will still occur when the depth-integrated defect production rate is balanced by the loss of defects at the receding surface, i.e., $j_a = 0$ in Eq. (3) but the sign of the term $j_i Y$ is reversed. Consequently, the point defect density and the differential volume free-energy density between grains will become ion flux energy independent. Such flux density dependence of grain growth and reorientation rates will then only result from the influence of thermal spikes. Experimental evidence on the dependence on grain curvature is not conclusive since, as Alexander and Was[48] observe, this rate has been variously estimated to have a curvature dependence ranging from zero to between the second and third power, and so no decision as to the more likely driving process can yet be reached for the case of postdeposition ion-irradiation-induced growth or reorientation of grains. However, it is possible that this range of exponents for the curvature dependence is indicative of the simultaneous operation of primary and secondary recrystallization mechanisms. In both model approaches for this postdeposition system, an identical dependence of growth upon ion flux density is predicted, as are dependencies upon F_D and Q, so experimental variation of any of these parameters and observations of changes in grain growth rate alone will be unable to distinguish between the mechanisms, whereas observations of grain reorientation rates will allow this distinction to be made.

The only other analytical approach to grain reorientation resulting from ion assistance during deposition appears to be that of Bradley, Harper, and Smith,[49] who assumed that the deposition process continuously produced randomized material but the channeling effect resulted in a lower sputtering yield for aligned material, so that material oriented within the critical channeling angular range grew more rapidly than that outside this range. The term ‘‘material’’ is used deliberately here, since the analysis was not concerned with the evolution of specific grains as in the present and other analyses described above. Since the model assumes a competition between randomization from the deposition process and orientational selection due to differential sputtering rates, it was clear that the analysis should predict a time dependence of the orientational selection and that, in general, complete orientation uniformity would not result. The orientational order at any time or deposited thickness, including the final steady state, was found to increase with increasing ion-to-depositing-atom arrival rate ratio r, provided that net deposition still occurred and with the fraction of orientations for which channeling was allowed. The steady-state degree of orientational order was determined to be a nonlinear function of r and the relaxation time to approach this steady state exhibited a peaked distribution as a function of increasing r. The former prediction was in qualitative agreement with experimental studies by Yu *et al.*[28,29] of azimuthal reordering of Nb films deposited with 200 eV Ar^+ ion assistance, but no studies were available to confirm the latter prediction. The steady state of incomplete orientational order is clearly different from the present analytical predictions, but it should be noted that under the low-energy ion irradiation conditions used in the experimental work there could be a distinct possibility of competing surface migration effects, which could attempt to drive the system to the minimum surface free-energy density configuration. This, in fact, will be generally true even when high-energy ions are employed, since there will always be an energy deposition in the near-surface region which can accelerate the tendency toward minimum surface free-energy geometry and compete with mechanisms that drive the system toward optimum channeling geometry.

The nonlinearity of the behavior of orientational order with r is also predicted in the present work, but the experimental data available are insufficient to allow comparison with either the present or the Bradley, Harper, and Smith[49] predictions. Since their studies involved only differentials in sputtering yield as the cause of orientational reordering, and no influence of thermal spikes, there were no explicit dependencies on ion energy or substrate temperature involved in these predictions. Consequently, a possible way of evaluating the merits of these approaches would be a systematic study of grain reorientation rates as functions of these parameters as well as more detailed investigation of the role of the ion-to-atom arrival rate ratio.

Turning now to comparison of the present models with experimental work it is, unfortunately, the case that little structured investigation has so far been undertaken. As indicated in the Introduction the ion-irradiation-induced grain reorientation studies by Dobrev[26] and Van Wyk and Smith[27] led to the concepts of channeling-related defect production differentiation and thermal spike acceleration of grain reorientation employed in the present analysis, but no significant ion parameter or substrate temperature variation was undertaken nor were explicit measurements of reorientation rates made with which to compare the present work. These studies were undertaken with relatively high-energy ions in the tens of keV range, whereas the investigations by Yu *et al.*[28,29] used much lower-energy ion irradiation. Similarly, low-energy studies of the ion-assisted deposition of Ag films were undertaken by Kay, Parmigiani, and Parrish,[32] in which it was observed that for films deposited without ion assistance the preferred texture was parallel to $\{111\}$ planes, those of minimum surface free-energy density. As the energy per deposited atom was increased there was, initially, an increase in the presence of more open $\{200\}$ planes, but for energies per atom above 42 eV the fraction of these orientations decreased. Although the increasing fraction of low-index planes is consistent with the channeling-related effects discussed here, and the initial increase in this fraction with energy per deposited atom is in qualitative agreement with the present analysis, the subsequent reduction in this fraction is not in accord with our analysis. However, the authors of Ref. 32 note that the film thicknesses grown for different ion assistance conditions vary and that as thickness increases relaxation of lattice strain, not considered in the present work, may be influential.

Further low-energy studies have revealed[2,87] that in the deposition of Al on SiO_2 in the presence of 2 keV Al^+ ion bombardment and a value of $r \sim 0.01$ an increased close-packed texture resulted, and more recent studies of the same system but in which self-ions of Al were employed and where both the ion energy and r were varied independently have been reported.[88] In these studies the degree of $\{111\}$-oriented texture increased continuously with increasing ion energy up to 120 eV and r up to 0.68 for an ion energy of 34 eV. Subsequent studies of the self-ion-assisted deposition of Cu on Si and Ge substrates,[89] however, showed an increased tendency for the development of preferred $\{001\}$ orientational texture when growth occurred on either $[100]$- or $[110]$-oriented substrates. Despite lattice mismatch in such cases there will be, of course, a tendency toward heteroepitaxial growth. Neither of these studies is fully compatible with the present analysis, and Kim *et al.*[88] argued that, in the low-energy ion range used in their work, a major factor was the increased nucleation density and smaller island sizes resulting from ion bombardment, and that ion impact onto such incipient grains could induce their recrystallization toward more favored low surface free-energy density conditions. To some extent, therefore, this mechanism is not unlike the low-energy surface thermal-spike-mediated grain reorientation process considered here, but operating even before columnar growth commences. In the case of Cu deposition, it was suggested[89] that a major effect of congruent ion irradiation was in the relaxation of misfit strain between the film and substrate, again a process not included in this present approach, and in addition as ion energy was increased to above about 50 eV thermal spike effects reduced the defect density by enhancing defect annealing rates.

It is rather clear, from this brief summary of experimental studies of preferred-orientation grain evolution with low-energy ion assistance, that the present approach is incomplete and that, as indicated earlier, the early stages of atomic nucleation before columnar growth starts may be influential, together with consideration of the effects of misfit and its relaxation between film and substrate, in describing the initial state of the columnar structure. Once this has developed, however, it is reasonable to believe that the current approaches, even in the low-energy ion case, may become increasingly applicable, and that investigations of all stages of texture evolution as films thicken would be advantageous. For higher ion energies, on the other hand, these early-stage processes may become of increased significance, and the present analysis can be considered as a step forward in providing a theoretical justification of the concepts of volumetric free-energy density minimization and the influence of thermal spikes.

VII. CONCLUSIONS

In summary, the study has developed a hierarchy of models to explain the tendencies of granular structures formed by ion-assisted atomic deposition of films to exhibit preferred orientation texture. For low-energy ions it was suggested that thermal spike effects would enhance the isothermal process of driving the system to one of the lowest surface free-energy density but, for higher-energy ions, differences in channeling fractions between differently oriented grains would lead to surviving defect densities and the ensuing tendency to minimize volume free-energy density. It was shown that these free-energy densities could, for reasonable experimental conditions, be comparable to other sources of free-energy density, and that thermal spike processes could considerably enhance grain growth and reorientation rates. A methodology for predicting these reorientation rates was developed. It was also shown that a transition from low- to high-energy conditions may occur at which the granular evolution changes from surface- to volume-dominated effects and an estimation of the transition energy was made. In practical terms thermal-spike-mediated effects are expected to be of greater significance when medium energy and large ion and film atomic masses are used. Reorientation rates are predicted to be nonlinearly dependent on the ion-to-atom arrival rate ratio and upon power-law functions of ion energy, and will increase with increasing channeling fraction and defect survival probability. Additionally, system temperature will be a decisive factor in determining the dominant reorientation process, since increasing this temperature will enhance purely thermal processes relative to thermal spike effects and reduce differential channeling fractions and defect survival probabilities, with the result of enhancing the role of surface-related processes. Qualitatively, therefore, it may be anticipated that channeling-related mechanisms may be dominant for higher-energy ions at lower temperatures. Unfortunately, there is no currently available systematic experimental data set with which to compare these predictions, and it is suggested that such investigations would be valuable, in which the parameters identified here as being relevant are controllably varied and the different reorientation regimes explored.

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