Pattern formation by ion–assisted alloy deposition

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MAX-PLANCK-GESELLSCHAFT

Introduction

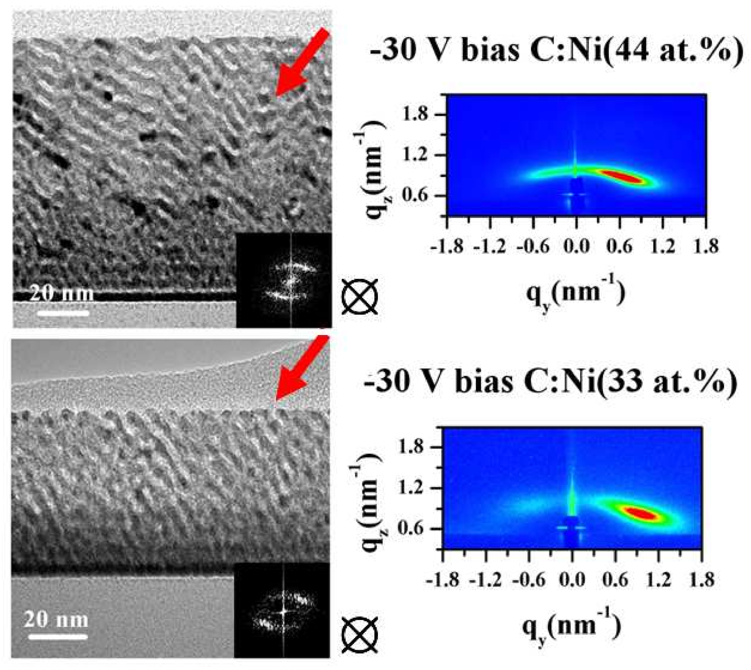
Film growth shows many instability types:

- dynamic instabilities due to interaction of impinging species with surface
- kinetic instabilities if growth of surface faster than its equilibration
- thermodynamic instabilities
- geometric instabilities due to shadowing

Ions irradiation huge impact on structural properties, alternative ways to grow materials

- nanostructured surfaces with tunable surface roughness/composition patterns composed from a material different than that of the substrate
- 3D compositional nanopatterns or nanocomposites with tunable structural properties (periodicity, composition, tilt...)

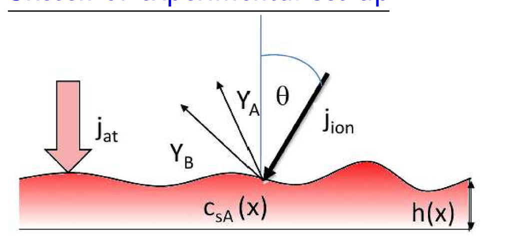
Ionized-PVD



Abrasonis et al. J. Appl. Phys. 108, 043503 (2010)

Model development

Sketch of experimental set up



Depositing atomic fluxes F_A and F_B under a bombarding ion flux $I\cos(\theta)$

•local height $h(x,y)$ exhibits atomic density $\rho_S(x,y)$ with local surface atomic fraction $c_{S,i}(x,y)$, $i=A,B$
•depositing flux $F=F_A+F_B$, atomic flux $j_{\rm at}=(c_{0,A}F+c_{0,B}F)\,S/\rho_s$ where $c_{0,B}=1-c_{0,A}$
•irradiating ions induce sputtering Y_i

I. Mass conservation law

Time evolution of the film surface height $h(x,y)$

$$\frac{\partial h}{\partial t} = \frac{\Delta}{\rho_S}(F_AS_A+F_BS_B)\,\hat z-\Delta\left(\frac{I\cos(\theta)}{\rho_S}\bar Y+\Delta\nabla\cdot\mathbf{j}\right) = j_{\rm at}\Delta-j_{\rm ion}\Delta\bar Y-\Delta^2\nabla\cdot\mathbf{j}$$

where Δ monolayer thickness or atomic diameter
•Sputtering or surface atomic redistribution removes atoms of the type B (A) and atoms from underlying layer $h(x,y)-\Delta$ become atoms of the surface
•local surface composition changes only if uncovered atoms from bulk are of type A (B)
Mass conservation law for surface atomic fraction $c_{S,A}(x,y)$

$$\frac{\partial c_{s,A}}{\partial t}=j_{\rm at}(c^0-c_{s,A})-(1-c_{b,A})\,(c_{s,A}j_{\rm ion}Y_A+\Delta\nabla\cdot\mathbf{j_A}) +c_{b,A}\left[(1-c_{s,A})j_{\rm ion}Y_B+\Delta\nabla\cdot\mathbf{j_B}\right]$$

where $c_{b,A}=c_{S,A}(x,y,h(x,y)-\Delta)$ atomic fraction at the underlying layer

II. Planar film growth

•Homogeneous film growth $h=h_0+Vt$, $c^0_A(h-\Delta)=c^0_{S,A}$, yields $c^0_{S,A}=\frac{1}{2RY}\left[1+RY-\sqrt{(1+RY^2-4c^0RY}\right]$ where $Y=Y_A-Y_B>0$ preferential sputtering of one specie
•ion-to-atom arrival ratio $R=\frac{j_{\rm ion}}{j_{\rm at}}=\frac{(F_AS_A+F_BS_B)}{I\cos(\theta)}$ order parameter

III. Deposition-induced surface redistribution fluxes

•deposition flux $F_i=F_i^0\left(1+a_{ST,i}\nabla^2h(x,y)+\ldots\right)$ where $a_{ST,i}<0$
•sticking coefficient $S=S^0\left(1+a_S\nabla^2h(x,y)+\ldots\right)$ where $a_S>0$
•Downward funneling $\mathbf{j_{ne,i}}=-\frac{F_i^0S^0}{\rho_S^0}a_{DF,i}\nabla h(x,y)+\ldots$ where $a_{DF,i}>0$ mobility of funneled atoms
•Trapping of atoms on slope $\frac{1}{\rho_S}=\frac{1}{\rho_S^0}\left(1+a_{SD}\nabla^2h(x,y)+\ldots\right)$ where $a_{SD}<0$ defects which trap atoms
Together $\frac{\partial h}{\partial t}\approx j_{\rm at}\Delta-j_{\rm ion}\Delta\left[c_{S,A}Y_A+(1-c_{S,A})Y_B\right]-\Delta^2(\nabla\cdot\mathbf{j}_\mathbf{A}^{\rm dep}+\nabla\cdot\mathbf{j}_\mathbf{B}^{\rm dep})$
with $\mathbf{j}_i^{\rm dep}=-\frac{F_i^0S^0}{\rho_{S,0}}\left(a_{ST,i}+a_S+a_{DF,i}+a_{SD}\right)=-c_{0,i}j_{\rm at}S_i^{\rm dep}\nabla h$

IV. Ion irradiation - induced fluxes

•relocation currents $\mathbf{j}_i^{\rm rel}=-c_{S,i}j_{\rm ion}S_i^{\rm rel}\left\{S_x^{\rm rel}(\theta)\frac{\partial h}{\partial x},S_y^{\rm rel}(\theta)\frac{\partial h}{\partial y}\right\}$
•sputtering can depend on local surface curvature $Y_i=Y_i^0\left[1+\upsilon_0\frac{\partial h}{\partial x}-S_x^{\rm sp}(\theta)\Delta\frac{\partial^2h}{\partial x^2}-S_y^{\rm sp}(\theta)\Delta\frac{\partial^2h}{\partial y^2}\right]$

V. Diffusive currents

•concentration gradients and surface 'stiffness' or capillarity with atomic volume Ω, surface energy γ: $\mathbf{j_i}^{\rm diff}=-\Delta D_i\rho_S\nabla c_{S,i}+c_{S,i}\frac{\Delta D_i\rho_S\Omega\gamma}{k_BT}\nabla(\nabla)^2h$,

G. Abrasonis, K. Morawetz, PRB sub: *Instability types at ion-assisted alloy deposition: from two-dimensional to three-dimensional nanopattern growth*, arXiv:1109.5461
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Final set of equation

$h=h_0+Vt+u(x,y), c_{S,A}=c_S^0+\phi(x,y)$, changing variables $\tau=j_{\rm at}t$, expressing height and spatial coordinates in units of $U=u/\Delta$, $x\to\Delta x$

$$\frac{\partial U}{\partial\tau}=-R\upsilon\frac{\partial U}{\partial x}+RS_x\frac{\partial^2U}{\partial x^2}+RS_y\frac{\partial^2U}{\partial y^2}-RY\phi+D\nabla^2\phi-B\nabla^4U$$
$$\frac{\partial\phi}{\partial\tau}=-\phi-RY^*\phi-R\upsilon^*\frac{\partial U}{\partial x}+R\left[S_x^*\frac{\partial^2U}{\partial x^2}+S_y^*\frac{\partial^2U}{\partial y^2}\right]+D^*\nabla^2\phi-B^*\nabla^4U$$

with $R=j_{\rm ion}/j_{\rm at}$ and coefficients

$$\begin{aligned}
Y&=(Y_A^0-Y_B^0) & Y^*&=(1-c_S^0)Y_A^0+c_S^0Y_B^0\\
\upsilon&=\upsilon^0[c_S^0Y_A^0+(1-c_S^0)Y_B^0] & \upsilon^*&=c_S^0(1-c_S^0)\upsilon^0(Y_A^0-Y_B^0)\\
D&=(D_A-D_B)\,\rho_S/j_{\rm at} & D^*&=\left[(1-c_S^0)D_A+c_S^0D_B\right]\rho_S/j_{\rm at}\\
B&=\left[c_S^0D_A+(1-c_S^0)D_B\right]\rho_S\Delta^2\gamma/k_BTj_{\rm at} & B^*&=c_S^0(1-c_S^0)\,(D_A-D_B)\,\rho_S\Delta^2\gamma/k_BTj_{\rm at}
\end{aligned}$$

total curvature-dependent displacement/deposition:

$$\begin{aligned}
S_{x,y}^{\rm ion}&=S_{x,y}^{\rm sp}(\theta)\left[c_S^0Y_A^0+(1-c_S^0)Y_B^0\right]+S_{x,y}^{\rm rel}(\theta)\left[c_S^0S_A^{\rm rel}+(1-c_S^0)S_B^{\rm rel}\right]\\
S_{x,y}^{\rm dep}&=c^0S_A^{\rm dep}+(1-c^0)S_B^{\rm dep}\\
S_{x,y}&=S_{x,y}^{\rm ion}+S_{x,y}^{\rm dep}/R
\end{aligned}$$

preferential curvature-dependent displacement/deposition:

$$\begin{aligned}
S_{x,y}^{*,ion}&=c_S^0(1-c_S^0)\left[S_{x,y}^{\rm sp}(\theta)\left(Y_A^0-Y_B^0\right)+S_{x,y}^{\rm rel}(\theta)\left(S_A^{\rm rel}-S_B^{\rm rel}\right)\right]\\
S_{x,y}^{*,\rm dep}&=c^0(1-c_S^0)S_A^{\rm dep}-c_S^0(1-c^0)S_B^{\rm dep}=c^0(1-c^0)(S_A^{\rm dep}-S_A^{\rm dep})+(c^0-c_S^0)S_{x,y}^{\rm dep}\\
S_{x,y}^*&=S_{x,y}^{*,\rm ion}+S_{x,y}^{*,\rm dep}/R
\end{aligned}$$

Stability analyzis

consider $(U,\phi)=(U^0,\phi^0){\rm e}^{ikx+rt}$, with growth rate r as eigenvalues of

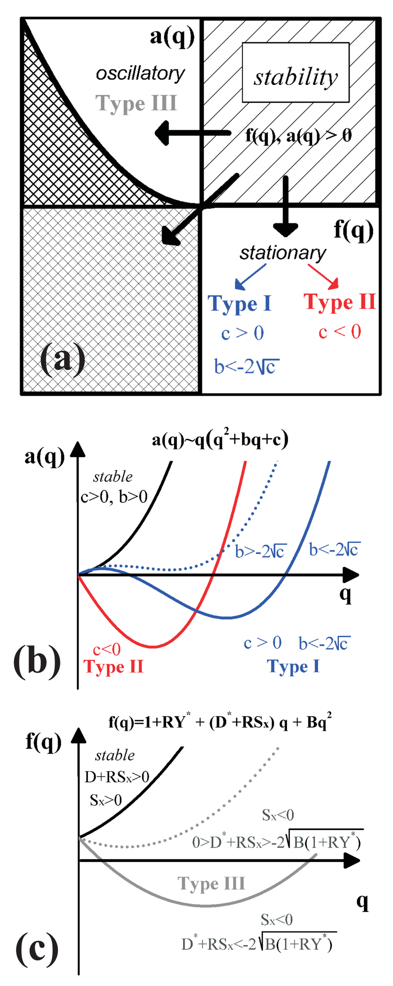
$$\mathbf{A}=\begin{pmatrix}-RS_xk^2-Bk^4 & -RY-Dk^2\\ -RS_x^*k^2-B^*k^4 & -1-RY^*-D^*k^2\end{pmatrix}$$

with eigenvalues

$$\begin{aligned}
r&=\frac12\left(-f(q)\pm\sqrt{f(q)^2-4a(q)}\right),\\
f(q)&=-tr\mathbf{A}=B\left(d+e\,q+q^2\right)\\
a(q)&=\det\mathbf{A}=f_{\rm dis}\,q\left(c+b\,q+q^2\right),
\end{aligned}$$

$k^2=q\geq0$ and the auxiliary quantities

$$\begin{aligned}
f_{\rm dis}&=BD^*-B^*D=\frac{\rho_S^2\gamma\Delta^2}{k_BTj_{\rm at}^2}D_AD_B>0\\
b&=\frac{B+R(S_xD^*-S_x^*D+BY^*-B^*Y)}{f_{\rm dis}}\\
c&=\frac{R\left[S_x+R(S_xY^*-YS_x^*)\right]}{f_{\rm dis}}\\
d&=\frac{1+RY^*}{B}>0\\
e&=\frac{D^*+RS_x}{B}.
\end{aligned}$$



•Growth rate r negative (stable) if $a(q)>0$ which is fulfilled in the absence of deposition and ion irradiation since always $f_{\rm diss}>0$
•Stationary patterns if $f(q)>0$ and $a(q)$ changes sign, range $q_0^\pm=\frac12\left(-b\pm\sqrt{b^2-4c}\right)$, two real q for $c<0$ or $c>0$, $b<-2\sqrt c$
•Oscillation if $f(q)<0$ or $e<-2\sqrt d$, or $RS_x<-\left(2\sqrt{B(1+RY^*)}+D^*\right)$

Ion-irradiation induced instabilities

Type IIa: curvature-dependent displacement-driven pattern formation

$c<0$ for two possibilities $S_x\lesseqgtr 0$ bandwidth from $k=0$ of unstable modes $\Delta k^2=\Delta q\approx-R\frac{S_x}{B}+o(R^2)$, maximal growth rate $k^2_{\rm max}=q_{\rm max}=\frac13(\sqrt{b^2-3c}-b)\approx-R\frac{S_x}{2B}+o(R^2)$, most unstable wavelength diverges when $R\to0$ while band width shrinks as $\sim\sqrt R$ (type-II instability) characteristic for ripple formation during ion erosion, $S_x<0$ further restrictions $R<R_{\rm crit,1}$

Type IIb: preferential curvature-dependent displacement and sputtering.

$S_x>0$ total curvature-dependent displacement stabilizes surface, element segregation occurs on surface as preferentially displaced element is depleted from crests and enriched in depressions $RS_x^*\frac{\partial^2U}{\partial x^2}$, preferential sputtering of same element occurs $-RY\phi$, and depressions resulting in increase of surface roughness, close to instability threshold $R=R_{\rm crit,1}+\delta$ and $\Delta k^2=\Delta q\approx\frac{S_x}{f_{\rm dis}b_{\rm crit}}\delta$
(i) *instabilities can be generated by ion-induced* $h(x,y)$-$c_S(x,y)$ *feedback interactions*, (ii) *strength of ion-induced feedback interactions is driven by differences of material ballistic properties*

Type I: preferential curvature-dependent displacement and diffusion

$c>0$ and $b<-2\sqrt c$ follows $R>R_{\rm crit,2}$ given by $b^2=4c$, positive (negative) S_x^*: preferentially displaced element is depleted from crests (depressions) and accumulates in depressions (crests) $RS_x^*\frac{\partial^2U}{\partial x^2}$, segregation induces concentration gradient between crests and valleys, diffusion homogenize element distribution on surface $D\nabla^2\phi$, preferential diffusion from depressions increase surface roughness, instability threshold $R=R_{{\rm crit}-2}+\delta$, band width $\Delta k_x=\sqrt{\Delta q}\sim\delta^{1/4}$ and $k_{\rm max}\approx\sqrt{-\frac16b_{\rm crit}+\frac{const}{|b_{\rm crit}|}\times\delta}$
external preferential ion-induced curvature-dependent processes and material-inherent diffusive processes couple to induce instability

Oscillatory instability

$f(q)$ changes sign from positive to negative while $a(q)>0$: r imaginary $fore<-2\sqrt d$ and $c>0$; $b^2<4c$, for $e<0$, total curvature-dependent displacement yields S_x must be negative, thus destabilizing, $R>R_{\rm crit,3}$ defined by $e^2=4d$, band width $\Delta k^2=\Delta q\sim\delta^{1/2}$, $k^2_{\rm max}=q_{\rm max}=-\frac e2\sim-\frac{e_{crit}}{2}-\frac{S_x}{2B}\delta$
oscillating instability establishes self-organized 3D-multilayer structure, ion-irradiated surfaces during alloy film growth can induce not only lateral but also vertical periodic structures

Deposition-induced instabilities

In the absence of ion irradiation only two types of instabilities, type IIa and type I, *no oscillatory instability can be reached at perpendicular atom incidence due to curvature-dependent deposition effects*
•band width $\Delta k^2\approx-\frac{S^{\rm dep}}{B}\sim j_{\rm at}$, fastest growing wave number $k^2_{\rm max}\approx-\frac{S^{\rm dep}}{2B}\sim j_{\rm at}$
•critical deposition flux $j_{\rm at,crit}$, near threshold $j_{\rm at}=j_{\rm at,crit}+\epsilon$ and $\Delta k_x\sim\epsilon^{1/4}$
•similarly to ion-induced instability, smoothing effect of the deposition dynamics and diffusion separately stabilize surface to obtain narrow band of unstable wave numbers where ordered structure is formed

Phase diagrams

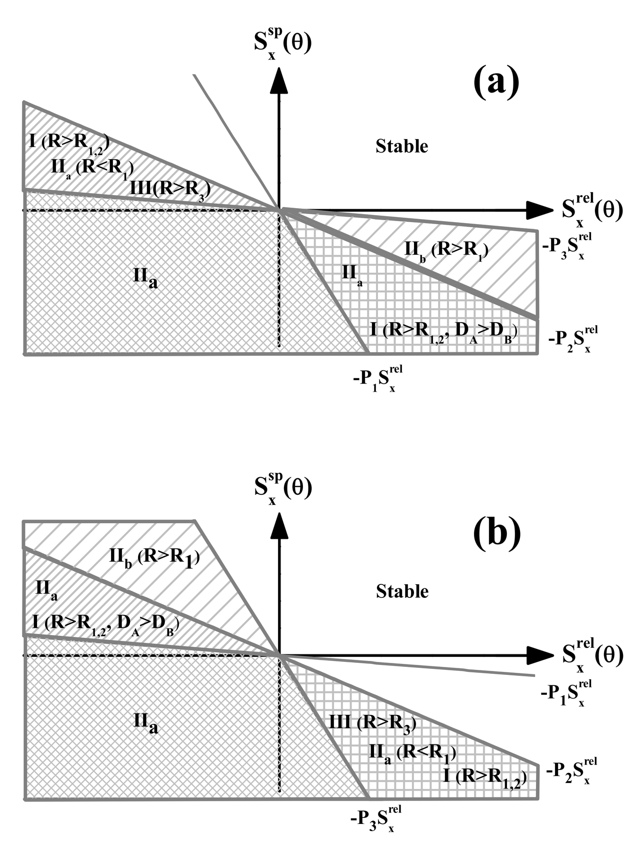
three positive combinations of relocation and sputtering,

$$P_1=\frac{S_A^{\rm rel}-S_B^{\rm rel}}{Y_A^0-Y_B^0},\ P_2=\frac{c_S^0S_A^{\rm rel}+(1-c_S^0)S_B^{\rm rel}}{c_S^0Y_A^0+(1-c_S^0)Y_B^0},\ P_3=c_S^0\frac{S_A^{\rm rel}}{Y_A^0}+(1-c_S^0)\frac{S_B^{\rm rel}}{Y_B^0}$$

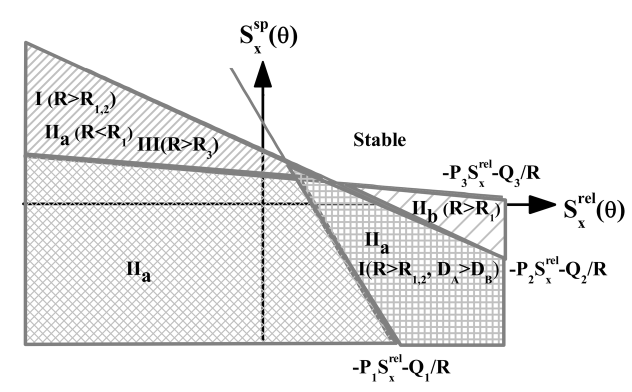
with $P_1\gtrless P_2\gtrless P_3\leftrightarrow Y_A^0S_B^{\rm rel}\lessgtr Y_B^0S_A^{\rm rel}$
Inclusion of deposition $S_x^{\rm rel}P_i\to S_x^{\rm rel}P_i+\frac{Q_i}{R}$ with

$$Q_1=\frac{\frac{c^0}{c_S^0}S_A^{\rm dep}-\frac{1-c^0}{1-c_S^0}S_B^{\rm dep}}{Y_A^0-Y_B^0},\ Q_2=\frac{c^0S_A^{\rm dep}+(1-c^0)S_B^{\rm dep}}{c_S^0Y_A^0+(1-c_S^0)Y_B^0},\ Q_3=c^0\frac{S_A^{\rm dep}}{Y_A^0}+(1-c^0)\frac{S_B^{\rm dep}}{Y_B^0}$$

where $Q_1\gtrless Q_2\gtrless Q_3\leftrightarrow Y_A^0\frac{1-c^0}{1-c_S^0}S_B^{\rm dep}\lessgtr Y_B^0\frac{c^0}{c_S^0}S_A^{\rm dep}$



Phase diagram of different types of instabilities for relocation to sputtering ratio $\frac{S_A^{\rm rel}}{Y_A^0}>\frac{S_B^{\rm rel}}{Y_B^0}$ (a) and $\frac{S_A^{\rm rel}}{Y_A^0}<\frac{S_B^{\rm rel}}{Y_B^0}$ (b)



Phase diagram for preferential relocation to sputtering ratio of species A, deposition effects are included considering the case of preferential curvature-dependent deposition to sputtering ratio of species A which shifts all axes by the corresponding Q values

Summary

Ion irradiation during film growth has a strong impact on structural properties. Linear stability analysis is employed to study surface instabilities during ion-assisted growth of binary alloys. An interplay between curvature-dependent ion-driven and deposition-driven instabilities is investigated. We demonstrate that ion irradiation of growing binary alloys leads to the formation of composition-modulated surface patterns. It is shown that the ion-to-atom arrival ratio R is the pattern control parameter. Close to the instability threshold we identify different regimes of instabilities driven by ion- or deposition-induced surface roughness processes, or roughness-composition feedback interactions. In particular, the synergistic effects of the curvature-dependent displacement and deposition coupling to the preferential sputtering or to the preferential diffusivity are found to induce instabilities and pattern formation. Depending on the film growth and ion-irradiation conditions, the instabilities show stationary or oscillating behavior. The latter one is exclusively connected with ion irradiation. The corresponding phase diagrams are presented in terms of experimentally accessible parameters. This shows an alternative way to control surface patterning and to grow three-dimensional laterally or vertically ordered nanostructures.