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Nanoscale precipitation patterns in carbon–nickel nanocomposite thin films: Period and tilt control via ion energy and deposition angle

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Periodic precipitation patterns in C:Ni nanocomposites grown by energetic ion codeposition are investigated. Films were grown at room temperature by ionized physical vapor deposition using a pulsed filtered cathodic vacuum arc. We reveal the role of the film composition, ion energy and incidence angle on the film morphology using transmission electron microscopy and grazing incidence small angle x-ray scattering. Under these growth conditions, phase separation occurs in a thin surface layer which has a high atomic mobility due to energetic ion impacts. This layer is an advancing reaction front, which switches to an oscillatory mode, producing periodic precipitation patterns. Our results show that the ion induced atomic mobility is not random, as it would be in the case of thermal diffusion but conserves to a large extent the initial direction of the incoming ions. This results in a tilted pattern under oblique ion incidence. A dependence of the nanopattern periodicity and tilt on the growth parameters is established and pattern morphology control via ion velocity is demonstrated. © 2010 American Institute of Physics. [doi:10.1063/1.3467521]

I. INTRODUCTION

Nanocomposite thin films have attracted a significant attention due to their multifunctionality and the fact that the material properties cannot be predicted from the properties of their constituents alone. However, control over the structure at the nanoscale level remains one of the major challenges. Self-organization at the nanoscale is of great interest as it promises a potential bottom-up route to the nanostructure control. In contrast to self-assembly where the periodic structures occur when approaching thermodynamic equilibrium, self-organization occurs via the interplay between two factors—an external constraint acting on an internal ordering mechanism.¹ Reaction-diffusion induced spatiotemporal periodic structures are a prototypical system in which chemical reactions are limited by a diffusion process,^{2,3} examples of these are chemical oscillators⁴ or Turing patterns.^{5–7} Thus, Liesegang patterns occur due to periodic precipitation in the wake of the reaction front.^{2,8–12} Originally observed as inorganic salt precipitation in a gelatin matrix,¹³ the Liesegang concept is generalized to a matrix where bulk diffusion limited periodic precipitation occurs.^{2,14} The periodicity is determined by the reaction front velocity v (i.e., the diffusivities of the reactive species) and the diffusivity D of the precipitating phase atoms.¹⁴ Attempts to generate periodic precipitation patterns have been pursued for more than 100 years.^{3,8,9,15–17} A major challenge to the use of periodic precipitation for the bottom-up approach in materials design, however, is the control of the motion of the reaction front and of the precipitation kinetics.^{3,14,16–18} Bulk diffusion during growth of physical-vapor and chemical-vapor deposited

inorganic thin films is usually too small to initiate a Liesegang mechanism. Therefore, in this case structure evolution can occur only by an interplay of surface ad-atom mobility, surface reactions, and the coverage rate,^{19–23} resulting usually in dispersed nanoprecipitates or columnar nanoparticles.

Recently, Liesegang-like nanoscale periodic precipitation patterns parallel to the surface were observed in films grown by deposition of energetic ions, whereby hyperthermal energy is provided in a near-surface region due to energetic (~ 10 – 100 eV) ion impacts.^{24–27} Incoming energetic ions induce atomic displacements along their path due to collisions.^{28,29} This results in collision-induced random walks of atoms in the near surface layer defined by the ion range.²⁵ A constant supply of ions results in a steady-state movement of the surface. The phase separation kinetics is confined to the moving surface layer, leaving the precipitation patterns “frozen” in the bulk. The depth of this “active” layer may be adjusted by changing the ion energies and masses, providing external control of the pattern periodicity.^{25,27}

In this study, the phase separation during the C:Ni film growth under energetic physical vapor deposition (PVD) conditions is studied. Although the two elements form a metastable Ni_3C ,^{30,31} excess carbon is quickly expelled from the carbide phase. The influence of film composition, the energy and incidence angle of incoming species on the film morphology is investigated. The control over the energy and direction is achieved using ionized PVD (iPVD)^{30–32} in the form of multicathode pulsed filtered cathodic vacuum arc (PFCVA). Phase separation at these energetic growth conditions results in the self-ordering of metal precipitates. Moreover, we show that these periodic precipitation patterns can be tilted in a controlled manner using oblique ion incidence.

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The Liesegang-like metal nanopatterns align no longer with the advancing surface but with the incoming ions.

II. EXPERIMENTAL DETAILS

A. Film synthesis

The depositions were performed onto thermally oxidized (SiO_2 layer thickness of ~ 500 nm) Si substrates using following two PFCVA systems: one at the University of Sydney, Australia (details are described elsewhere^{33–35}) and another built according to Sydney's prototype at the University of Linköping, Sweden. Each arc pulse deposits less than one monolayer of one kind of ions, resulting in composites from sequentially pulsed cathodes. For the former system, an arc current of ~ 1.5 kA was used with pulse lengths of 0.3 ms for Ni and 0.8 ms for C at the pulsing frequency of 3 Hz. Base pressure was 1.3×10^{-6} mbar or lower. A curved magnetic filter was used to remove the droplets and neutrals from the depositing flux, with a magnetic field strength of ~ 15 mT and ~ 47 mT for the C and Ni cathodes, respectively. Depositions were performed by repeating C and Ni pulse sequences from 6:1 to 3:2 in order to get the total carbon pulse number equal to 1866. This results in the carbon areal density of $\sim 7 \times 10^{17}$ atoms cm^{-2} and the Ni atomic ratio in the range of 6–43 at. %. Note, for the PFCVA system at the University of Linköping, the technical growth parameters were adjusted to obtain similar film compositions.

The most probable native kinetic energies of incoming carbon and nickel ions are ~ 20 eV and ~ 40 eV, respectively, while the average charge states are approximately +1.0 and +1.8, respectively, according to measurements made on similar systems by Anders and Yushkov.³⁶ Note that the native kinetic energies and average charge states of C and Ni ions could be somewhat higher than the estimates given from the work of Anders and Yushkov³⁶ because of the significantly higher currents employed in the cathodic arc system used in this work. Although in the low current regime these parameters are independent of the arc current,³⁷ once the cathode current increases to values over 1 kA they are observed to increase with increasing arc current.³⁸ This is believed to be due to the high self-magnetic fields generated by the high currents flowing in the micrometer sized cathode spots. These fields lead to increased confinement of the spot plasma and delay the transition to a nonequilibrium plasma with “frozen-in” charge states as does the application of an external magnetic field.^{36,38–40}

In addition to the natural Ni and C ion energies, an additional acceleration occurs when approaching the sample surface which is proportional to the difference between the plasma potential (V_p) and the substrate potential (V_s). The plasma potential is estimated to be approximately ~ 10 V.³³ For a number of experiments V_s was fixed at -15 or -30 V, while for the angular dependence depositions the substrate was allowed to float. Based on the structure investigation of unbiased and biased samples at otherwise identical growth conditions we estimate the floating potential to be on average below -10 V throughout the pulse.

When the sample is placed in the system without additional tilting the incoming plasma makes an angle of $\sim 15^\circ$

from the substrate normal (designated as $+\sim 15^\circ$). In order to achieve perpendicular incidence the sample holder was tilted toward the plasma beam by 15° (designated as $\sim 0^\circ$). Depositions were also performed tilted a further 15° away from the plasma ($+\sim 30^\circ$) and 30° toward the plasma ($-\sim 15^\circ$).

B. Characterization

The total amount of deposited Ni and C was determined by combined Rutherford backscattering spectroscopy (RBS)—nuclear reaction analysis measurements using 1.2 MeV deuterium ions. The nuclear reaction $\text{C}^{12}(d,p)\text{C}^{13}$ cross section exhibits a maximum at approximately this deuterium ion energy, significantly enhancing the proton signal from carbon, while RBS of deuterium from the heavy nickel atoms measures the Ni content in the deposited layer (for more details see Ref. 41).

The morphology of the films was studied by transmission electron microscopy (TEM) and grazing incidence small angle x-ray scattering (GISAXS). TEM investigations were carried out on cross-sectional samples employing FEI Titan (operated at 300 kV) and FEI Tecnai G2 TF 20-UT electron (operated at 200 kV) microscopes. Two-dimensional (2D) GISAXS measurements were recorded by means of a charge coupled detector at the Rossendorf Beamline ROBL BM 20, at the ESRF, Grenoble, France. The x-ray beam with wavelength $\lambda = 0.1051$ nm arrives at the sample with an incidence angle α_i which was kept above the critical angle of total external reflection at 0.3° or 0.35° in order to probe the all of the C:Ni precipitate layers. The reported GISAXS features can be observed only when the angle of incidence is larger than the critical angle. The in-plane scans were carried out at the beamline ID01 at the ESRF, Grenoble, France, using x-ray radiation of wavelength $\lambda = 0.1127$ nm and a position sensitive detector (PSD). The PSD wire was aligned parallel with the sample surface so that the in-plane information could be measured with one shot (for more details see Ref. 41).

III. RESULTS AND DISCUSSIONS

Ion impacts normal to the surface result in an alternating carbon rich and nickel rich layered structure [cross-sectional TEM (XTEM) image, Fig. 1(a)]. This is in accordance with results reported in the literature.^{25,33} The layers consist of individual carbide nickel nanoparticles in a carbon matrix. The undulations of Ni concentrations within each layer are correlated with the Ni distribution in adjacent layers, indicating that nanoparticle nucleation is dependent on the morphology of the underlying layer.

Ion impacts off-normal to the surface tilt the alternating carbon rich and nickel layers [Figs. 1(c), 1(e), 1(g), and 1(i)], and the Ni precipitate layers tend to align normal to the ion beam direction. At the very beginning of the deposition process a few precipitate layers form parallel to the substrate surface before the layers tilt. An increase in both Ni content and ion energy reduces the tilt angle and increases the period. After tilting the sample, the fast Fourier transform (FFT) of the XTEM images exhibit rotational rather than mirror symmetry. The orientations of the most intense peaks

FIG. 1. (Color online) C:Ni film morphologies by XTEM (left column) and GISAXS (right column). Growth parameters are indicated on the corresponding panels. The arrows in right up corners of the XTEM images schematically indicate the incoming ion direction. The insets are FFTs of the corresponding XTEM images. The crossed circles indicate the direction of the x-ray beam for the corresponding GISAXS measurements. The azimuthal angle $\phi \approx 0$, thus $q_x \approx 0$.

match the direction of the incoming ions [cf. rather symmetrical FFTs of horizontal layers in Fig. 1(a)].

2D GISAXS images [see Figs. 1(b), 1(d), 1(f), 1(h), and 1(j)] represent essentially the Fourier transformation of the density contrast autocorrelation function.⁴² Taking into account that the incidence and scattering angles are small, the horizontal and vertical components of the scattering vector $\mathbf{q}(q_x, q_y, q_z)$ are expressed as

FIG. 2. (Color online) 2D GISAXS images measured at $\alpha_i = 0.35^\circ$ of the C:Ni (~ 50 at. %) films grown at ion incident angles of $\sim 30^\circ$ (a), $\sim 15^\circ$ (b), $\sim 0^\circ$ (c), and $\sim -15^\circ$ (d).

$$q = \frac{2\pi}{\lambda} [\sin \phi \sin 2\theta_{sc} \cos \alpha_{sc}, \cos \phi \sin 2\theta_{sc} \cos \alpha_{sc}, \sin \alpha_i + \sin \alpha_{sc}], \quad (1)$$

α_i is the x-ray angle of incidence, α_{sc} and θ_{sc} are out-of-plane and in-plane scattering angles, respectively, ϕ is the in-plane rotation angle (for more details see Ref. 41). 2D GISAXS images from a macroscopic sample region ($\sim 5 \text{ mm}^2$) closely resemble the upper part of the FFT patterns of the local area probed by TEM, confirming that the observed asymmetries are a global property of the material [Figs. 1(b), 1(d), 1(f), 1(h), and 1(j)]. The influence of the ion incidence is highlighted in Fig. 2 as follows: the GISAXS lobe at positive q_y values moves counter-clockwise when the incidence angle decreases, passes through zero at a perpendicular incidence and appears in the negative q_y range for the ion incidence of -15° (for more details see Ref. 41). Note, that no ordered structures have been observed for the Ni content of ~ 7 at. %, and 2D GISAXS shows no detectable density contrast (not shown).

Frequency-filtered XTEM images of a C:Ni (~ 32 at. %) sample are shown in Fig. 3. This film is thicker than that presented in Fig. 1(d). The periodic composition modulations observed in the original image [Fig. 3(a)] are enhanced when the Fourier components in the quadrants containing the incident ion direction are retained [Fig. 3(c)]. In the opposite case (the FFT quadrants in ion direction are removed) a weak periodic structure is also revealed. Thus the periodic composition modulations consist of two components: an intense composition modulation wave toward the

FIG. 3. (Color online) Detailed morphology of a C:Ni (~32 at. %) sample (ion incidence $\sim 15^\circ$ incidence, bias -30 V). (a) is the XTEM image and the FFT of the C:Ni layer (inset); (b) and (c) are filtered XTEM images (frequency masks in the insets); (d)–(h) are GISAXS images obtained at x-ray incidence angle of $\alpha_{in}=0.30^\circ$ ($\lambda=0.1051$ nm) after rotating the sample around its normal by an angle ϕ (Note that $|q_r|=\sqrt{q_x^2+q_y^2}$); (i) is a ϕ scan at the fixed values of $\alpha_{in}=0.26^\circ$ and $q_z=0.83$ nm^{-1} ($\lambda=0.1127$ nm). The negative q_r values in (d)–(h) correspond to the positive values q_r in (i) for $\phi \geq 180^\circ$.

direction of the incoming ions and a weaker composition wave roughly perpendicular to the ion direction. This is reflected in the corresponding GISAXS image [Fig. 3(d)] where in addition to the intense lobe at the positive q_r values, a lobe of weak intensity at negative q_r values is also observed. Note that a weak intensity lobe is observed in all asymmetric GISAXS patterns except for the C:Ni film with the lowest metal to carbon ratio of ~ 15 at. %. Thus, we

FIG. 4. (Color online) Characteristic period L (a) and layer tilting angle β (b) as determined from GISAXS (ion incidence $\sim 15^\circ$). Values in dark (light) circles correspond to the more (less) intense lobe.

attribute the intensity lobes to the distribution of the composition modulation waves within the films.

GISAXS images are presented in Figs. 3(d)–3(h) showing the C:Ni (~32 at. %) sample rotated about the surface normal by an angle ϕ [see Fig. 3(a) for geometry]. The information in these images may be considered analogous to FFTs of TEM cross-sections cut at corresponding angles ϕ . As the sample is rotated the two lobes also rotate counter clockwise and their intensities equilibrate at an orientation close to $\phi = -90^\circ$ (i.e., perpendicular to the plane containing the surface normal and incoming ion direction). This indicates that in the direction perpendicular to the incoming ions the structure is not stratified along the film growth direction but consists of oblique density modulations with similar periods, off-set angles and amplitudes. The latter strongly indicates that the metal rich layers observed by XTEM consist of individual nanoparticles and not continuous layers. Following this, the continuous layer appearance in XTEM must be attributed to projection effects (see also Ref. 25). The GISAXS pattern inverts under further rotation of the sample to $\phi = -180^\circ$, consistent with the above hypothesis. An in-plane scan at fixed $\alpha_i=0.26^\circ$ and $q_z=0.83$ nm^{-1} is shown in Fig. 3(i). The weak lobe does not contribute at this q_z value. The intensity is concentrated in the azimuthal angle range of $\sim -10^\circ < \phi < \sim 45^\circ$ with the maximum at $\phi \sim 23^\circ$. The fact that the maximum is not at $\phi = 0^\circ$ possibly relates to the fact that the incident ion flux leaves the arc filter at a certain azimuthal angle.

The vector joining the maximum of the lobe with the center of the reciprocal space q_{max} in 2D GISAXS images is inversely proportional to the modulation period $L=2\pi/q_{max}$ while the angle β which q_{max} makes with the central specular rod represents the tilting angle of the layers. The L and β values are summarized in Fig. 4. L increases concomitantly with the metal content and ion energy, while β shows the opposite tendency. Note that the period is always greater for the weak density modulation component, while the opposite is true for the value of the offset angle β .

The TEM micrographs and GISAXS data unambiguously demonstrate the existence of tilted periodic layers of nickel carbide nanoparticles in a carbon matrix whose tilt angle is correlated with the incident direction of the depositing ions. To explain the physical origin of this observation we first consider the periodic precipitation scenario in the absence of tilt as described by Gerhards *et al.*²⁵ for binary systems (metal:carbon) of depositing hyperthermal ions. Thermally activated diffusion processes are assumed to play a negligible role. In fact, low bulk diffusion in the film is a requirement to freeze-in the far-from-equilibrium state of the final nanostructure.^{25,33} Any considerable surface diffusion destroys the periodic precipitation pattern³³ and results in the formation of columnar structures.^{19,20,22,23,33,43} During film growth, short-range ballistic displacement of atoms takes place in a near-surface region ($\sim 1\text{--}2$ nm thick) due to hyperthermal ion impacts.^{28,29} Thermodynamic forces lead to a precipitation of metal carbide or pure metal phase in the carbon matrix.^{24–26,33,43,44} Carbon ions continue to be deposited onto the carbon matrix or onto the clusters themselves. Eventually excess carbon segregates to surfaces of and spaces between the clusters, encapsulating the metal and forming a continuous carbon layer. The nickel nanoparticles capture metal atoms in their surrounding thus creating nickel depleted zones. This prevents any competing precipitation in the immediate nickel nanoparticle vicinity as the nickel concentration threshold necessary for an effective nucleation cannot be reached.⁴⁵ This provides a negative feedback which is another self-organization prerequisite.¹ Additional metal ions are sub-planted into the clusters until the carbon surface layer reaches a critical thickness at which the metal atoms no longer reach the buried clusters. New nickel enriched zone builds up which upon reaching the threshold value results in the precipitation of the next layer,⁴⁵ and the process repeats. This is consistent with the experimental results that no ordered structures have been observed for low Ni contents: ballistic diffusion length determined by the energy of incoming ions is too small to induce segregation of appreciable amounts of Ni into small localized regions which are necessary to initiate precipitation. Note, that the resputtering plays a negligible role for compound forming nanoparticles as in the present case of nickel carbide.²⁵

In explaining the tilting of the patterns by oblique ion incidence, we consider the trajectories of the energetic ions. Depending on the ion impact location, an ion travels through a carbon rich or nickel rich medium. Binary collision simulations using the SRIM 2008 code (the Stopping and Range of Ions in Matter⁴⁶) show that significant deviations from the initial straight trajectory occurs due to atomic collision and the initial direction is almost lost in the equal mass subsystems (Ni^+ in Ni or C^+ in C) [see Figs. 5(a) and 5(b)]. This results in a shallow ion penetration with the straggling comparable to the penetration depth. The effect is amplified in the case of a light ion traveling in a heavy matrix such as carbon in nickel. On the contrary, little deviation occurs during the movement of heavy energetic particles in the medium consisting of light atoms. As the latter process conserves the initial directionality to the largest extent it is assumed to be the driving mechanism transferring the direction of the in-

FIG. 5. (Color online) Ion mediated self-organization mechanism during the growth. Carbon (50 eV) (a) and nickel (100 eV) (b) ion depth distribution in different environments calculated by SRIM 2008. Schematic growth stages at the perpendicular (c) and oblique (d) ion incidence. Dark circles represent newly subplanted Ni atoms at a given stage while gray ones represent metal segregated into nanoparticles. Shaded areas represent carbon matrix. Carbon ions (not shown in the schemas) are assumed to be codeposited and result in the advancing surface.

coming ions into the tilting direction of the precipitation patterns. The metal ions traverse the material until they encounter a metal rich region whereby they are captured; the shadows behind these regions are metal-poor. This provides a positive feedback mechanism characteristic for self-organization processes;¹ metal rich regions are further enriched due to their larger stopping power. Under oblique angle incidence these metal rich zones form sideways from the nickel nanoparticles which results in the nucleation and growth of tilted layers [compare Figs. 5(c) and 5(d)]. The lateral position of the new nucleation zone depends on the projected thickness of the carbon phase which depends on the metal/carbon ratio in the incoming flux. Larger incoming metal ion energy results in a larger subplantation depth which is consistent with the observed increase in the periodicity L as a function of the substrate bias (see Fig. 4). The accompanied decrease in the pattern tilting angle β is consistent with the fact that the increase in the ion energy by substrate bias increases the perpendicular to the surface component of incoming ion momentum. Since the substrate is smooth and homogeneous the patterning must develop during the film growth, consistent with the observation of a transition layer.

Alternatively, the precipitation pattern tilting under oblique ion incidence can be due to anisotropy in ion induced diffusion. It is known that the atomic displacement average of the energetic ion induced collision cascade exhibits a larger component in the incoming ion direction.⁴⁷ Such a process can be translated into the anisotropy of the diffusion tensor $\mathbf{D}(\mathbf{r}-\mathbf{v})$. This results in the ion induced mass transport being different in the directions parallel and perpendicular to the incident ion direction. In this case, the process does

not depend on the mass difference between composite constituents but on the general properties of the ion induced ballistic processes. Discrimination between these two mechanisms requires further experimental and theoretical studies. However, in both cases, the active kinetic layer is defined by the thickness of the ion induced ballistic displacement zone. The latter is controlled externally by the ion energy and incoming angle and defines an effective diffusion coefficient D .⁴⁷ The D/v ratio determines the average random-walk distance and thus the pattern periodicity.

IV. CONCLUSION

Self-organization during the iPVD growth of C:Ni nanocomposite thin films has been studied by means of TEM and GISAXS. The issues of the influence of metal content, incoming ion energy and incidence angle have been addressed.

It has been shown that the energetic PVD results in the formation of nanoscale precipitation patterns of metallic nanoparticles. The formation of the ordered structures requires a critical metal amount. We have demonstrated that the directionality of the incoming ions is transferred to the periodic precipitation process during iPVD, and the precipitation nanopatterns tilt under oblique ion incidence. The periodicity and tilt are caused by ion induced ballistic effects and, consequently, depend on the ion energy, ion incidence angle and incoming flux composition. Our findings suggest that energetic ion deposition offers means for the external and independent control of the precipitate atom diffusivity D , the front movement velocity v and pattern tilt via incoming ion energy, material supply rate and incidence angle, respectively.

Similar effects are expected from alternative iPVD techniques such as ion beam deposition, pulsed laser deposition, or high-power pulse magnetron sputtering, as well as for various types of matrices (e.g., BN (isoelectronic to carbon), oxides or metals) and different dispersed phases with pronounced optical (e.g., Au or Cu) or magnetic properties (e.g., Fe, Co, CoPt, FePr). These expectations are supported by previously reported vertical composition modulations during perpendicular iPVD or ion assisted growth of carbon-transition metals,^{24–26,33} Au–SiO₂⁴⁸ or Au–Ni.²⁷ Moreover, changing the tilting or in-plane angle during growth provides the potential to sculpt the patterns into complex structures such as chevrons and helices. Previously reported sculpting using glancing angle deposition^{49,50} utilizes very low energy atomic deposition resulting in free standing structures. Protecting those structures from degradation requires a post-growth filling of the empty space between the nanoparticles. In contrast, the nanoparticles presented here are automatically encapsulated during the growth. This opens new avenues for the bottom-up synthesis of nanostructured materials with controlled three-dimensional ordering.

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