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Structure formation in Ag-X (X = Au, Cu) alloys synthesized far-from-equilibrium

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Abstract

We employ sub-monolayer, pulsed Ag and Au vapor fluxes, along with deterministic growth simulations, and nanoscale probes, to study structure formation in miscible Ag-Au films synthesized under far-from-equilibrium conditions. Our results show that nanoscale atomic arrangement is primarily determined by roughness build up at the film growth front, whereby larger roughness leads to increased intermixing between Ag and Au. These findings suggest a different structure formation pathway as compared to the immiscible Ag-Cu system, for which the present study, in combination with previously published data, reveals that no significant roughness is developed, and local atomic structure is predominantly determined by the tendency of Ag and Cu to phase-separate.
I. Introduction

Atomic arrangement and, by extension, physical attributes of multicomponent thin films synthesized from the vapor phase are set by the complex interplay among thermodynamic driving forces that either promote or hinder miscibility and compound formation, kinetic barriers that determine rates of atomic-scale structure-forming processes, and the arrival pattern of vapor species at the film growth front.\(^1\)\(^-\)\(^3\) Recently, we developed a research methodology which encompasses flux modulation with sub-monolayer resolution, nanostructure probes, and deterministic growth simulations, allowing us to understand the way by which this interplay affects structure formation within the binary Ag-Cu model system.\(^4\)

Inherent to the Ag-Cu binary alloy is that its constituents are *immiscible* over the entire composition range in their solid state.\(^5\) This means that phase separation is an intrinsic feature that enhances compositional modulation, making it easier to obtain experimental information at the nanoscale that can be correlated with simulations. In the present study, we explore the viability of the research methodology explained above at more challenging conditions by studying the fully *miscible* Ag-Au system\(^6\) that does not exhibit an inherent tendency towards phase separation. In addition, Ag-Au is a common binary alloy for use in bimetallic nanostructures where the atomic arrangement at the interface between Ag and Au can be used to tailor e.g., optical properties.\(^7\)\(^-\)\(^10\)

Our results show that atomic arrangement in Ag-Au is predominantly governed by roughness build up at the film growth front—as determined by the kinetic conditions and the arrival pattern of the film forming species—whereby larger roughness
promotes intermixing between Ag and Au. This is in contrast to the Ag-Cu system, which we also revisit in the present study, for which roughness is significantly smaller and atomic arrangement is primary controlled by the tendency of Ag and Cu to segregate. The methodologies presented herein can be used for studying atomic arrangement and interfacial structure in technologically relevant ceramic alloys.

II. Research strategy

A. Thin film growth and characterization

Films were grown epitaxially on MgO (100) single-crystalline substrates. This approach was chosen to avoid formation of polycrystalline films and by extension minimize the complexity of characterization by electron microscopy (see later in the present section). All depositions were carried out in a multi-source, ultra-high vacuum chamber at a base pressure of \( \sim 10^{-7} \) Pa and vapor was generated from magnetron sputtering sources operating at an Ar gas pressure of 0.67 Pa. The Ag target (purity 99.99 at.\%) was placed 12.5 cm away from the substrate and at a \( \sim 40^\circ \) angle with respect to the substrate surface normal. The latter was also the case for the Au target (purity 99.99 at.\%), but the target-to-substrate distance was instead 7.5 cm. Both targets were 7.6 cm in diameter, the Ag target was 6 mm thick, while a 1.6 mm thick Au target bonded to an equally thick Cu backing plate was used.

The growth sequence commenced by degassing the MgO substrates at 650 °C followed by the deposition of a \( \sim 20 \) nm thick TiN layer at the same temperature in order to improve the epitaxial quality of the subsequent film.\(^{11}\) TiN layers were grown by supplying pulses with a frequency of 1 kHz, a width of 100 µs and a time-averaged power of 250 W to a Ti target (purity 99.95 at.\%)—being at a \( \sim 40^\circ \) angle and 7.5 cm
distance with respect to the substrate—in an Ar-N$_2$ atmosphere at a total pressure of 0.67 Pa. The samples were then allowed to cool down to room temperature in a load-lock chamber with a base pressure of $\sim$10$^{-6}$ Pa. After cooling down, a $\sim$30 nm thick Ag film was deposited on top of the TiN layer using pulses with a time-averaged power of $\sim$2 W, a width of 50 µs, and a frequency of 1 kHz.

Ag-Au films were subsequently grown using a, by us, recently developed synthesis technique $^4, ^{12}, ^{13}$ that utilizes multiple power supplies to generate electrical pulse trains and sequentially activate spatially separated magnetrons. Each pulse within a pulse train has a typical width 10 to 100 µs and results in a deposition rate of the order of 10$^{-4}$ to 10$^{-2}$ monolayers (ML) per pulse. This means that the amount of material deposited during each pulse train can be controlled with sub-monolayer resolution by changing the number of pulses ($N_p$) comprising the pulse train. In the present study, this method was employed using alternating Ag and Au pulse trains, whereby $N_p^{\text{Ag}}$ and $N_p^{\text{Au}}$ were varied in the respective ranges 1000-20000 and 500-10000 pulses. The pulse width was set to 50 µs, the pulsing frequency to 1 kHz, and the time-averaged power was $\sim$2 W for both Ag and Au targets. These conditions resulted in vapor arrival rates per pulse of $\sim$5$\cdot$10$^{-4}$ and $\sim$10$^{-3}$ ML for Ag and Au, respectively, as determined by x-ray reflectivity measurements of monolithic Ag and Au films deposited at the same conditions, as the alloy Ag-Au films, on Si (100) substrates covered by a thermally grown SiO$_2$ layer. Based on this we expect that the number of Ag or Au atoms deposited during each pulse train correspond to a range $\sim$0.5 to $\sim$10 ML, where 1 ML refers to the number of atoms comprising a Ag (100) plane. For reference, films were also grown by co-depositing continuous vapor fluxes at similar, to the pulsed process, time-averaged deposition rates. To increase the efficiency of sample characterization,
each sample was grown as a stack comprising five to six layers deposited at different pulse train length conditions. The different layers were separated by a 10 nm thick Ag film—grown at the same conditions as the Ag film deposited on top of the TiN layer—to provide a similar starting surface for and allow identification of each layer in electron microscopy analysis.

To determine the effect of different growth conditions on atomic arrangement, microstructure, and composition, samples were investigated by means of high resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray spectroscopy (EDS-STEM). Prior to analysis, cross-sectional specimens were thinned to electron transparency by a two-step procedure consisting of mechanical polishing followed by Ar⁺ milling at a shallow incidence angle of 6° measured from the sample interface, using gradually decreasing ion energies; 5 keV initially and then followed by 2.5 keV and finally 1 keV. HRTEM analyses were carried out in a FEI Tecnai G² TF 20 UT instrument operated at 200 kV. HAADF-STEM and EDS-STEM data were collected using a probe-corrected and monochromated FEI Titan³ 60-300 microscope equipped with a high-brightness XFEG source operated at 300 kV. EDS maps were recorded with a Super-X EDS detector system for ultra-high-count rates in STEM mode. This enables a total number of counts well above 1.000.000 to be collected, which was done using ZAF correction and k-factor method yielding an accuracy of ~2 at.%. We also extracted line-scan intensity profiles by integrating measured counts for each element over the entire width of EDS-STEM maps every ~0.1 nm along the film growth direction.
B. Growth simulation details and analysis

To complement experimental data on Ag-Au structure and allow for comparison with the Ag-Cu system, growth of Ag-X (X=Au, Cu) films on Ag (100) and (111) surfaces was simulated by molecular dynamics (MD) using a Finnis-Sinclair Ag-Au-Cu interatomic potential. As substrates, Ag fcc boxes oriented along the [100] and [111] directions were used. The respective box sizes were 17.2 x 17.2 x 4.5 nm$^3$ and 17.4 x 17.6 x 4.3 nm$^3$ containing 77616 and 75600 atoms. These box sizes were chosen for obtaining sufficient statistics of key atomic-scale processes during film growth, while maintaining computational efficiency. For both boxes, the bottom half of the atomic layers were kinetically frozen to resemble the bulk atoms, whereas the top half of the layers were kept at a constant temperature of 500 K using a Nose-Hoover thermostat to represent the substrate surface. In order to mimic the experimental use of pulse trains, film growth was simulated by releasing pulses of atoms at random distances between 6 and 12 Å above the substrate every 150 ps; test simulations showed that this time was sufficient to allow for relaxation of the growing film surface between material pulses. Deposited atoms were given an initial velocity, perpendicular to the substrate, that corresponds to an average kinetic energy of 800 K and were further accelerated by the attractive force of the surface atoms once their distance from the surface became smaller than the cut-off radius of the interatomic potential (~5.3 Å). The initial deposited atom energy of 800 K in the simulations is smaller than the typical values of ~10000 K of sputtered species. This choice was made in order to minimize ballistic effects of deposited atoms on the growing surface and selectively study the effect of pulse modulation of film morphological evolution. Each pulse consisted of 5% of a ML of the same element and the number of pulses in each pulse train was adjusted to deposit atoms corresponding to 0.5-6 ML of each element at global at.%
compositions Ag:X equal to 50:50 and 35:65. One monolayer is here equal to the number of atoms in the topmost Ag substrate layer, i.e., 3528 and 4200 for the (100) and (111) surfaces, respectively. In total, 24 ML were deposited for each condition. In addition, simultaneous deposition of Ag and X atoms was simulated for reference.

The simulated structures were visually inspected using the Ovito software. To allow for a more direct comparison with the EDS data, the normalized elemental composition profile along the z-axis was extracted from the simulations by determining the number of atoms of each element in the x-y plane for every 0.2 nm along the out-of-plane z-direction. The number of Au atoms was then subtracted from the number of Ag atoms and normalized to the total number of atoms in 1 ML.

The evolution of the morphology at the growth front was evaluated by determining the surface width, $W$. This quantity is a measure of roughness and is calculated as

$$W^2 = \sum_{n=0}^{top} (n - \Theta)^2 \varphi_n$$

where $n$ is the atomic layer number and $\Theta$ is the total nominal thickness deposited (in ML). $\varphi_n$ represents the exposure of layer $n$ and is calculated based on the layer coverages $\theta_n$, $0 \leq \theta_n \leq 1$, according to the expression

$$\varphi_n = \theta_n - \theta_{n+1}. \quad (2)$$

In that way, if layer $n$ is completely covered by layer $n+1$ then $\varphi_n=0$, leading to a zero contribution of the corresponding term in Eq. (1). For perfect layer-by-layer growth this means that only two layers are contributing to the sum in Eq. (1), which in that case can be simplified to $W^2 = \theta_{top}(1 - \theta_{top})$. Thus, $W$ is zero when $\theta_{top}$ equals either 0 or 1 (complete layer) while it reaches a maximum value of 0.5 when $\theta_{top} = 0.5$ (half of the $n_{top}$ layer is filled). In the case of 3D growth, roughness develops at the growth front.
resulting in already-formed atomic layers to be filled out at a rate slower than that at which new layers are formed. Hence, the number of exposed layers increases causing $W$ to increase with $\Theta$.

III. Results and discussion

A. Ag-Au (100) thin film synthesis

Figure 1 (a) presents a HAADF-STEM overview micrograph of a Ag-Au stack grown on MgO (100). The stack contains films synthesized using alternating Ag and Au pulse trains with $N_{p}^{Ag}/N_{p}^{Au}$ values of 11600/6300, 7700/4200, 3900/2100 and 1900/1100 pulses, as well as a film grown by co-deposition with a 10 nm thick Ag film between each layer. For the sake of brevity, the different growth conditions are hereinafter noted using the respective $N_{p}^{Ag}$ value. All films are found to grow epitaxially on the MgO (100) substrate, as demonstrated by the HRTEM micrograph and its associated FFT pattern taken from the $N_{p}^{Ag} = 7700$ pulses layer (Figure 1(b)). Moreover, the growth front exhibits waviness, which appears to emanate from the surface of the Ag layer deposited on TiN and increases in amplitude along the stack growth direction.

The HADDF-STEM micrograph in Fig. 1(a) reveals that the total film thickness varies from 20 nm for the co-deposited case up to 44 nm for the film grown at $N_{p}^{Ag} = 1900$ pulses. During plasma ignition, before the power supply regulation has reached steady-state, a higher than set power is supplied temporary increasing the deposition rate. As the number of pulses in each pulse train increases, the influence of this effect decreases. Which is consistent with the thickness of the $N_{p}^{Ag} = 11600$ pulses condition, 34 nm, being 10 nm thinner compared to the $N_{p}^{Ag} = 1900$ pulses case. The differences in the film thickness affect also the film chemical composition with the Ag:Au at.% ratio
being 37:63, 35:65, 32:68 and 28:72 for the $N_{p}^{Ag}$ values 11600, 7700, 3900, and 1900 pulses, respectively. The corresponding at.% ratio for the co-deposited film is 44:56.

At low magnification (Fig. 1 (a)) a layered structure is observed for $N_{p}^{Ag}=11600$ and 7700 pulses, confirmed by the corresponding EDS map and the periodic oscillation of the integrated line-scan intensity profile for Ag and Au for the $N_{p}^{Ag}=11600$ pulses condition in Figs. 1 (c) and (d), respectively. From the EDS map and the intensity profile, the thicknesses of the individual Ag and Au layers are found to be ~2.1 and ~2.3 nm, respectively, with an interfacial region where mixing of the two elements occurs of typically ~0.6 nm width. Given the two elements' almost identical interplanar spacing of ~2.04 Å in the [100] direction, these layer thicknesses correspond to ~10 and ~11 lattice planes of Ag and Au, respectively. The layered structure exhibits clear signs of deterioration as $N_{p}^{Ag}$ is lowered to 3900 pulses (Fig. 1 (e)). Each layer is ~1 nm thick with the EDS map showing that Au is present throughout the Ag-rich layer and vice versa. This is consistent with the line-scan intensity profile plot in Fig. 1(f), which shows a decrease in the amplitude and the wavelength of the intensity oscillations. For $N_{p}^{Ag}=1900$ pulses in Figs. 1 (g) and (h), there is no sign of a layered structure, and full intermixing appears to have occurred with seemingly random distribution of Ag and Au atoms. This is also the case for the co-deposited film (not shown). Thus, decreasing the pulse train length changes the film structure from distinct multilayers, via seemingly intermixed multilayers, to an apparent random solid solution.

**B. Ag-Au (100) thin film growth simulations**

Cross-sections of simulated Ag-Au (100) film growth with a global Ag:Au at.% content of 50:50 and different amounts of atoms deposited per pulse train and element are
shown in Fig. 2, together with their corresponding normalized compositional intensity profiles along the z-axis. A multilayered structure with alternating layers of Ag and Au is observed for the 3 ML condition, as evidenced both in the simulation snapshots and by the periodic oscillations of the compositional intensity profile between nearly pure Ag and Au in Fig. 2(a). In addition, the interfaces between the layers are characterized by roughness. Moreover, post-simulation data analysis showed that the top substrate Ag layer contains ~4 % Au atoms which push Ag substrate atoms up into the film. Visual inspection of simulation movies revealed that the substrate-stemming Ag atoms do not extend beyond the first atomic layer in the film. The same type of intermixing was observed in the visualization of the simulations at all Ag-Au and Au-Ag interfaces of the structure that correspond to deposition of 3 ML per pulse train and element, but roughness makes quantification of this intermixing a non-trivial task. However, neither Au nor Ag is present on the top surface layer after deposition of a full pulse train of Ag or Au, respectively, indicating that the extent of intermixing is limited at the interface layer. This is in contrast to previous data on the immiscible Ag-Cu binary system where extensive trans-layer intermixing, mediated by near-surface exchange diffusion between Ag and Cu atoms, was observed.

Lowering the number of atoms per pulse train to 2 ML (Fig. 2 (b)) decreases the individual elemental layer thicknesses, while still maintaining the interfacial roughness. Compared to the 3 ML case, the amplitude and wavelength of the oscillations in the compositional intensity profile decreases even though single-element layers dominate. For 1 ML and co-deposition (Fig. 2 (c) and (d), respectively) the intensity oscillations vanish, and no signs of layering are observed. Growth simulations for global Ag:Au at% content 35:65 showed the same trends as those in Fig. 2 (not shown here). Thus,
in the remainder of the article only simulations for Ag:X (X = Au, Cu) at.% ratios of 50:50 are presented and discussed. All in all, we conclude that the structure evolution of the simulated Ag-Au (100) films qualitatively corroborates the experimental results presented in Section III.A. Hence, in the following section, simulations are used as a tool to elucidate key structure forming-processes.

C. Structure-forming processes and comparison to the Ag-Cu system

As noted in Section III.B for the simulated Ag-Au (100) cross-sections in Fig. 2 (a) and (b), the interfaces between Ag and Au layers are rough. Careful inspection of simulation visualization showed that this roughness is manifested by exposure of multiple atomic layers, e.g., after deposition of 2 ML ~4 layers are exposed. Based on the findings presented in Figs. 1 and 2 we suggest that structure formation in the Ag-Au (100) system is determined by this rough growth front, in a way described in the following.

For relatively long pulse train lengths, as those applied to achieve a multilayer structure in Fig. 1 (c) and Fig. 2 (a), each elemental layer covers those underneath. This means that atoms from the upcoming pulse train cover all exposed atomic layers of the underlying element, but the rough growth front causes intermixing at interfaces separating the elemental layers from each other as seen in Fig. 2 (a). By decreasing the pulse train length, the elemental layers get thinner and the roughness leads to intermixed layers (Fig. 1(e) and Fig. 2 (b)). Decreasing the pulse train length even further means that atoms deposited during the latest pulse train do not fully cover the surface underneath, leaving areas of the two elements exposed to the next vapor pulse. Applying a new pulse train allows arriving atoms to be deposited in or diffuse to
areas of the same element, such that elemental layers emanating from different pulse trains get interconnected. Through this process, the multilayer structure degenerates leading to a solid-solution (Fig. 1 (f) and Fig 2 (c)), as expected given the full miscibility of Ag and Au.$^6$

To probe that the mechanism suggested above for the structure evolution of Ag-Au (100) is also relevant for the (111) surface, additional growth simulations of Ag-Au (111) were performed. As a representative case for comparison, the cross-sectional view of a simulated Ag-Au (111) structure grown by depositing 2 ML per pulse train and element is presented in Fig. 3 (a), since this pulse train length coincides with the degeneration of a clear multilayered structure. The corresponding Ag-Au (100) structure, already presented in Fig. 2 (b), is also included for clarity in Fig. 3 (b). By comparing the two structures, a more pronounced intermixing can be seen for the (111) case, also evident by the lower amplitude in the oscillations of the elemental intensity profile for the (111) orientation, accompanied by larger roughness at Ag-Au interfaces and at the growth front. In contrast to Ag-Au (100), no Au atoms are directly seen in the Ag (111) substrate layer in Fig. 3 (a), while post-simulation data analysis revealed that only $\sim$1% of the top-most Ag substrate layer is penetrated by deposited Au atoms as compared to the $\sim$4% value found for the (100) surface.

Seeking to establish a more universal understanding of the fundamental processes controlling the atomic arrangement in miscible and immiscible Ag-based alloy films, we also simulated growth of Ag-Cu (100) and Ag-Cu (111) films by depositing 2 ML per pulse train and element (Fig. 4 (a) and (b), respectively). For both surface orientations, broken multilayer structures with little roughness are seen. The broken layers are
characterized by Ag clusters extending through multiple layers along the z-axis creating in-plane elongated Cu clusters surrounded by Ag, which is in good agreement with the data reported in Ref. [4].

From the visual inspection of Figs. 3 and 4, an apparent difference in roughness is observed between Ag-Au and Ag-Cu. In order to better understand this difference, the dynamic evolution of the growth front morphology is studied by calculating the surface width, $W$, using Eqs. (1) and (2) as a function of nominal thickness $\Theta$. The results are presented in Fig. 5 for the same 2 ML conditions as shown in Figs. 3 and 4. To make the effect of the modulated flux more clear, grey rectangles are added to the figure to mark the period during which Ag atoms are deposited. For Ag-Au (111) (blue dotted line), $W$ increases rapidly with nominal thickness reaching a value of 2.7 ML for 12 ML material coverage. This corresponds to an increase of the surface roughness that can be seen in the corresponding cross-sectional view in Fig. 3 (b). It is also in line with homo- and heteroepitaxial studies of the Ag-Au (111) system where multiple layers have been shown to arise prior to filling out the first.\textsuperscript{18–23} The evolution of $W$ for Ag-Au (100) (black solid line) does also show an overall increase with nominal thickness, but not to the same extent as for (111) as it only reaches a value of 0.88 ML at 12 ML material coverage. This is consistent with the behavior expected for fcc metals since the Ehrlich-Schwöbel barrier typically is found to be higher on the (111) surface as compared to the (100), leading to a rougher growth front in the case of (111).\textsuperscript{24–26} On the contrary, in the Ag-Cu films, $W$ initially increases and then saturates by oscillating around a value of $\sim$0.8 ML for both (100) (green dash-dotted line) and (111) surfaces (red dashed line). We suggest that this behavior may be caused by near-surface Ag diffusion processes—this type of diffusion has been suggested to drive phase
separation in the Ag-Cu system [4]—which can promote atom transport across layers mitigating differences in the Ehrlich-Schwöbel barriers for the two types of surfaces.

IV. Summary and outlook

We synthesized epitaxial (100) thin films within the miscible Ag-Au system using temporally modulated multiatomic vapor fluxes which were generated from spatially separated magnetron sources that were activated by electrical pulse trains. By decreasing the pulse train length $N_{pAg} (N_{pAu})$ on the Ag (Au) magnetron from 11600 (6300) down to 1900 (1100) pulses, so as to deposit less material in each pulse train, the structure changes from multilayers with a Ag (Au) layer thicknesses of $\sim 2.1 (\sim 2.3)$ nm, via intermixed multilayers where Ag- and Au- rich layers exhibit a thickness of $\sim 1$ nm, to solid solution. This evolution has been corroborated by MD growth simulations which show a transition from multilayer structures to an apparent solid solution when the amount of Ag and Au atoms deposited per pulse train length decreases from 3 down to 1 ML. Based on analysis of MD simulation data, we conclude that atomic arrangement is determined by the morphology of growth front during both Ag and Au deposition, yielding interfacial roughness between Ag and Au multilayers. For relatively short pulse train lengths the roughness causes exposure of the underlying layers that breaks the layer continuity causing an intermixed structure, and a solid solution at even shorter pulse train lengths. The formation of an even rougher growth front has been found for Ag-Au (111) by means of simulations and surface width calculations, as expected for fcc metals based on typical diffusion barriers values. These findings suggest a different structure-forming pathway as compared to the immiscible Ag-Cu system, in which no significant roughness is developed and atomic arrangement is primarily determined by the phase separation of Ag and Cu atoms.
The combined experimental and simulation approach presented herein can be used to study and unravel mechanisms that govern nanoscale self-organization in technologically relevant multinary compound films that comprise constituents with different degrees of miscibility. Notable examples are ternary ceramics based on group 4, 5, and 6 transition metal nitrides and AlN, including TiCrAlN\textsuperscript{27} and TiZrAl\textsuperscript{28} in which film mechanical properties and thermal stability strongly depend on atomic arrangement and interfacial structure between different phases.

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V. References


5 E. Ma, Prog. Mater. Sci. 50, 413 (2005).
10 J. Zhu, J. Li, and J. Zhao, Plasmonics 9, 435 (2014).
13 WO2015120893: Method of coating a substrate so as to provide a controlled in-plane compositional modulation, (2014).
Lett. 72, 3843 (1994).


Figure captions

Fig. 1. (a) HAADF-STEM micrograph of a Ag-Au (100) stack containing layers grown at pulse train lengths \( N_{pAg} \) equal to 11600, 7700, 3900 and 1900 pulses, as well as a layer grown by co-deposition (denoted by Co-dep). (b) HRTEM micrograph and associated FFT pattern as inset, taken from the layer grown at \( N_{pAg}=7700 \) pulses. (c), (e), and (g) EDS-STEM maps and (d), (f), and (h) integrated line-scan intensity profile along the film growth direction showing the compositional modulation induced by the different pulse train lengths applied in the Ag-Au (100) stack in (a). The EDS counts scale is the same in (d), (f), and (h). (c)/(d), (e)/(f), and (g)/(h) correspond to films growth for \( N_{pAg}=11600, 3900 \) and 1900 pulses, respectively.

Fig. 2. Cross-sectional view of simulated Ag-Au (100) film growth by depositing (a) 3 ML, (b) 2 ML, and (c) 1 ML per pulse train and element. (d) Cross-sectional view of simulated film growth by co-depositing Ag and Au atoms. The corresponding normalized elemental intensity profiles along the z-axis, calculated as explained in the text, are also presented next to each panel.

Fig. 3. Cross-sectional view of simulated Ag-Au structures together with their corresponding normalized elemental intensity profiles along the z-axis (calculated as explained in the text). (a) Ag-Au (111) and (b) Ag-Au (100) (previously presented in Fig. 2 (b)). Both simulations correspond to a deposition of 2 ML per pulse train and element.
Fig. 4. Cross-sectional views of simulated Ag-Cu structures. (a) Ag-Cu (100) and (b) Ag-Cu (111). Both simulations correspond to a deposition of 2 ML per pulse train and element.

Fig. 5. Surface width, $W$, calculated from Eq. (1) as function of nominal thickness deposited $\Theta$ for simulated Ag-Au (111) (blue dotted line), Ag-Au (100) (black solid line), Ag-Cu (111) (red dashed line) and Ag-Cu (100) (green dash-dotted line) structures. All data are extracted from simulations in which 2 ML per pulse train and element are deposited. The grey rectangles indicate to Ag deposition.
Figures

FIG. 1
FIG. 2
(a) Ag-Au (111)

(b) Ag-Au (100)

○ Au  □ Ag  ○ Ag substrate

FIG. 3
(a) Ag-Cu (100)

(b) Ag-Cu (111)

○ Cu  ○ Ag  ○ Ag substrate

FIG. 4
FIG. 5

Surface width, $W$ (ML)

Nominal thickness, $\Theta$ (ML)

- Ag-Au (111)
- Ag-Au (100)
- Ag-Cu (111)
- Ag-Cu (100)