Nanoscale Transition Metal Thin Films: Growth Characteristics and Scaling Law for Interlayer Formation

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ABSTRACT: A comprehensive study on the growth of nanoscale transition metal-on-transition metal (TM-on-TM) systems is presented. The near room-temperature intermixing and segregation phenomena during growth are studied in vacuo using high-sensitivity low-energy ion scattering. The investigated TM-on-TM systems are classified into four types according to the observed intermixing and segregation behavior. Empirical rules are suggested to qualitatively predict the growth characteristics of any TM-on-TM system based on the atomic size difference, surface-energy difference, and enthalpy of mixing between the film and substrate atoms. An exponential trend is observed in the effective interface width as a function of the surface-energy difference between the film and substrate layers, with a subtrend based on the crystal structure of the TM layers. A semiempirical model that accurately describes the experimental data is presented. It serves as a scaling law to predict the effective interface width and the minimum film thickness required for full film coverage in TM-on-TM systems in general. The ability to predict the growth characteristics as well as the interface width for any TM-on-TM system significantly contributes to the process of finding the best material combination for a specific application, where layer growth characteristics are implicitly considered when selecting materials based on their functional properties.

KEYWORDS: thin film growth, sputter deposition, interfaces, transition metals, intermixing, segregation, scaling law, low energy ion scattering

1. INTRODUCTION

Nanoscale transition metal (TM) thin films are widely used in several applications such as superconductors, semiconductors, magnetic, diffusion barriers, oxidation protective layers, and X-ray optics. Improvements in vacuum technology and deposition techniques, especially, the ability to deposit sub-nanometer thick layers, have been fueling the growth of thin-film-based technologies. When layer thicknesses reach the order of nanometers and sub-nanometers, the quality of the interface with adjacent layers becomes a key factor in realizing and further improving the device performance.

Nanoscale thin-film structures are generally designed to function near room temperature, where bulk diffusion of atoms is kinetically inhibited. Yet, intermixing with substrate atoms can easily occur during growth, even near room temperature, leading to wide interface profiles between the layers.1,2 This has become one of the limiting factors that restrains a thin-film structure from functioning at its maximum efficiency.3,4 With the help of current state-of-the-art characterization techniques, it is possible to do an in-depth analysis of interfaces and completely reconstruct the atomic concentration profiles with high accuracy.4,5 However, there is currently a limited capability to accurately predict the interface profile without having to deposit test structures and use advanced metrology for reconstruction. The availability of a scaling law to predict the interface profile between any two layers will add another dimension to the layer material selection process and, consequently, enable us to find the best material combination for the desired application.

The existing layer growth and segregation models6–11 cannot be used to predict interface profiles because of their dependence on energy terms (e.g., activation barrier and segregation energy) that can be obtained only from the experimental results of the specific material combination. Advancements in computational methods have made it possible to calculate the surface processes such as atomic

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exchange and adatom migration that take place during deposition.\textsuperscript{12−17} Recently, Roling and Mavrikakis\textsuperscript{17} compiled a database of calculated energies for adatom hopping and surface substitution in several TM systems. The database serves as a useful tool for a qualitative prediction of surface processes. Nevertheless, a quantitative prediction of the effective interface width due to intermixing during growth would require advanced simulations, which can become extremely time consuming and challenging. Although it is a laborious task to develop a general predictive model using computation methods, methodical experimental studies can be a viable alternative approach. Buchanan et al.\textsuperscript{1} presented an experimental study on intermixing between sputter-deposited aluminum and TMs. The authors reported a correlation between the intermixing length and cohesive energy of the TMs but were unable to present a model that explains the results. Given the absence of other extensive systematic studies on interlayer formation in the literature, it is the aim of this work to provide a generic database and develop a predictive model for intermixing in TM bilayer systems.

In this paper, we present an experimental data set on intermixing during layer growth in sputter-deposited transition metal-on-transition metal (TM-on-TM) thin films. The evolution of surface coverage during layer growth was systematically characterized using high sensitivity low-energy ion scattering (HS-LEIS), and the effective interface width values were extracted from the experimental data. A semi-empirical model is developed based on the surface energy and crystal structure properties of the TM layers to describe the intermixing process during growth. The values of the model parameters are obtained by fitting the experimental results.

2. THEORETICAL BACKGROUND

2.1. Surface-Exchange Model. Intermixing between film atoms and substrate atoms during deposition generally results in an intermixed zone between the layers. We consider intermixing to be the consequence of an exchange process between the film and substrate atoms during layer growth. This approach is similar to the two-state exchange model developed by Jorke\textsuperscript{9} to explain the surface segregation of Sb on Si(100) during molecular beam epitaxy growth. The following assumptions are made in our model:

(i) In the current study, the deposition is done near room temperature. The energy for atom mobility at the surface level comes only from the deposition process, with energy of the incoming film atoms on the order of \(\sim 10\) eV. Hence, the exchange process is considered to occur only between a surface atom and an underlying subsurface atom, whereas all atoms below the subsurface layer are considered to be part of the bulk and do not take part in the exchange process.

(ii) Surface-exchange processes are much faster than the timescale in which additional atoms arrive at the surface. This is certainly true for typical deposition rates on the order of sub-tenth nanometer per second and leads to a stationary state of surface and subsurface atoms before the arrival of the next atoms.

(iii) Near room temperature, diffusion of atoms in the bulk and desorption of atoms from the surface are negligible. The position of an atom is therefore final once it is buried under the subsequently deposited film atom.

(iv) Although \(\sim 10\) eV incoming film atoms do not induce resputtering,\textsuperscript{18} backscattered sputter gas neutrals with tens of eV energy can lead to resputtering of surface atoms. However, considering the typical low sputter yield up to \(\sim 100\) eV of incident energy and the low fraction of high-energy backscattered neutrals, the number of resputtered atoms must be negligible (if not completely absent) when compared to the deposited film atoms. Therefore, resputtering during growth is not considered in the model. Note that resputtering can become critical when low-energy ion treatment or substrate bias is used during deposition, and it may strongly affect the intermixing process.

(v) For the sake of simplicity, a typical 2D film layer growth is assumed without dewetting or island formation. This is a reasonable assumption, considering the negative enthalpy of mixing for most TM–TM combinations.\textsuperscript{19} The effects of positive mixing enthalpy on the surface morphology and intermixing process will be discussed in the Results and Discussion section.

We now consider two possible surface-exchange mechanisms during film deposition: deposition-induced exchange (Ex-1) and surface energy minimization-induced exchange (Ex-2). Ex-1 is caused by the ballistic collision between incident atoms and surface atoms. It may depend on several factors such as the energy of the incident film atom, bond energy, atomic mass, coordination number, and interatomic distance. Ex-1 is significant especially for deposition methods
with a high incident atom energy.\cite{13,14,15} Ex-2 is driven by the reduction in the surface-free energy of the system because of exchange in positions of the surface and subsurface atoms. It is well known that in an alloy, the element with the lowest surface energy tends to segregate from the bulk toward the surface,\cite{20,21} which is one of the ways to reduce the surface-free energy of the system. This is facilitated by bulk diffusion of atoms over long timescales and/or at elevated temperatures. In contrast, the deposition process takes place near room temperature and at short time scales. Thus, Ex-2 in general represents the exchange of atoms between the surface and subsurface layers because of surface-energy difference and not due to diffusion of atoms from the bulk.

A schematic representation of the surface-exchange model is shown in Figure 1. Incoming film atoms arriving at the surface have a certain probability of being implanted into the surface through the exchange mechanism Ex-1 (represented by atoms 1 and 2). Although the probability of exchange Ex-1 depends on the atomic composition near the site of arrival, it is not trivial to analytically express the exchange probability for each atom. As a result, we assume an effective probability of exchange Ex-1 ($\beta_1'$) for a given film–substrate material combination. Atoms that undergo Ex-1 are assumed to remain in the stationary state until the next impact. Film atoms that do not undergo Ex-1, given by an effective probability ($1 - \beta_1'$), ultimately diffuse laterally to another surface position near the site of impact (represented by atoms 3, 4, 5, and 6). The surface diffusion process is activated mostly by the excess kinetic energy of the incident atom,\cite{22} whereas the latent heat of condensation\cite{23,24,25} of the deposited film atoms can also contribute. The probability that a diffusing film atom stops on top of a substrate atom is equal to the coverage of the substrate atoms ($1 - \theta$), which is the fraction of surface area occupied by the substrate atoms. At this point, the film atom can either exchange its position with the underlying substrate atom through the Ex-2 mechanism (represented by atom 3) or remain stationary until the next impact (represented by atom 4). Again, an effective probability ($\beta_2'$) is assumed for the exchange Ex-2. Finally, the probability that a diffusing film atom stops on top of another film atom is equal to the coverage of the film atoms ($\theta$), which is the fraction of surface area occupied by film atoms. Like in the previous situation, the film atom can either exchange its position with the underlying film atom through the Ex-2 mechanism (represented by atom S) or remain stationary until the next impact (represented by atom 6). The effective probability of exchange Ex-2 between two film atoms is $\beta_2'$. It is important to note that out of all six cases described here, only the fourth case (atom 4 in Figure 1) contributes to a change in the film layer coverage ($\theta$). Consequently, the increment in film layer coverage ($d\theta$) for a small increment in deposition time ($dt$) can be expressed as

$$d\theta = \frac{\phi}{N_{sd}'}dt((1 - \beta_1')(1 - \theta)(1 - \beta_2'))$$

where $\phi$ is the deposition flux and $N_{sd}'$ is the surface atomic density of the film material; $\beta_1 = 1 - \beta_1'$ and $\beta_2 = 1 - \beta_2'$ for the sake of brevity. The deposited thickness ($h$) of the film layer for a deposition flux ($\phi$), deposition time ($t$), and volume density of the film atoms ($N_{sd}'$) is given by

$$h = \frac{\phi t}{N_{sd}'}$$

From eqs 1 and 2, the increment in film layer coverage for a small increment in the deposited film layer thickness ($dh$) can be expressed as

$$d\theta = \frac{N_{sd}'}{N_{sl}} dh \beta_1'(1 - \theta)$$

We get the expression for film layer coverage as a function of the deposited film layer thickness by integrating eq 3

$$\theta = 1 - e^{-\frac{N_{sd}'}{N_{sl}} \beta_1'}$$

During the deposition process, the surface is continuously bombarded by energetic incoming film atoms. This leads to an increase in temperature near the site of impact by up to several thousand kelvin, which is dissipated within a few picoseconds.\cite{15} The surface atomic exchange and diffusion processes activated by the impact of the incident film atom typically occur within the same timescale.\cite{13} Therefore, considering a quasi-thermal equilibrium at the surface level\cite{24,25} near the site of impact, for $n_i'$ number of deposited film atoms that did not undergo Ex-1 with substrate atoms, the ratio of number of these film atoms that move to the subsurface layer ($n_i''$) and stay at the surface layer ($n_i'$) because of exchange mechanism Ex-2 can be written as

$$\frac{n_i''}{n_i'} = e^{-\frac{\gamma_s - \gamma_f}{k_B T + \Delta E}}$$

where $\gamma_s$ and $\gamma_f$ are the surface energies of substrate and film atoms, $k_B$ is the Boltzmann constant, $T$ is the growth temperature, and $\Delta E$ is the additional energy available at the surface level because of the deposition process. Equation 5 implies that when $\gamma_s \ll \gamma_f$, most of the film atoms will move to the subsurface layer via the Ex-2 mechanism, which is in qualitative agreement with the relative trends in the calculated energies of substitution reported by Roling and Mavrikakis.\cite{17}

According to the assumptions (iii) and (iv)

$$n_i' + n_i'' = n_i'$$

The probability of a film atom staying at the surface without undergoing Ex-2 ($\beta_2'$) is then given by

$$\beta_2' = \frac{n_i'}{n_i'} = \frac{1}{1 + e^{-\frac{\gamma_s - \gamma_f}{k_B T + \Delta E}}}$$

$\beta_2'$ varies from 0 to 1 depending on the surface energies of the film and substrate atoms. By substituting eq 7 in eq 4, the expression for the film thickness $h_\theta$ required to achieve a certain film layer coverage $\theta$ can be derived as

$$h_\theta = -\ln(1 - \theta) \left[ \frac{N_{sd}'}{N_{sl} \beta_1'} \right] + e^{-\frac{\gamma_s - \gamma_f}{k_B T + \Delta E}}$$

$$h_\theta = -\ln(1 - \theta) A + e^{-\beta A}$$

where $A = (N_{sd}'/N_{sl} \beta_1')$ and $B = \left( \frac{1}{k_B T + \Delta E} \right)$ are the effective parameters with units of nm and 1/eV, respectively. The parameter $A$ denotes the intermixing due to ballistic collision and the parameter $B$, which is the inverse of the effective
thermal energy of the surface atoms, dictates the importance of surface-energy difference on the exchange mechanism Ex-2. When the effective thermal energy $K_0 T + \Delta E$ of the surface atoms increases, the surface-energy difference between the film and substrate atoms becomes less significant. For instance, it has been reported that Pt atoms (high surface energy) submerge under a Ge substrate layer (low surface energy) during room temperature deposition but emerge out at elevated temperatures.\textsuperscript{26} Both the parameters may depend on several crystal structure properties such as coordination number, nearest neighbor distance, lattice spacing, atomic packing, and stacking sequence.

### 2.2. Interface Profile Model

The interface profile between two layers is often mathematically represented by exponential, linear, sinusoidal, or error function (ERF).\textsuperscript{27} The most commonly used interface profile is the ERF profile\textsuperscript{28} given by

$$C(z) = \frac{1}{2} \left[1 - \text{erf}\left(\frac{z - z_i}{\sigma/\sqrt{2}}\right)\right]$$  \hspace{1cm} (10)

where $C$ is the concentration of the deposited film atom at a depth $z$ from the surface, $z_i$ is the point of inflection of the ERF, and $\sigma$ is the effective width of the interface. The integral of the concentration profile gives the deposited film layer thickness ($h$)

$$h = \int_0^\infty C(z) \, dz$$  \hspace{1cm} (11)

The effectiveness of ERF to describe the interface profile in thin films has been recently reported by Coloma Ribera et al.\textsuperscript{2} Nevertheless, it is complicated to analytically express the concentration ($C$) as a function of the deposited thickness ($h$). To overcome this problem, we propose to describe the interface profile by a logistic function (LGF)\textsuperscript{29}

$$C(z) = \frac{1}{1 + e^{(z - z_i)/0.59\sigma}}$$  \hspace{1cm} (12)

whose shape is similar to that of an ERF. The factor 0.59 within the exponent provides the best fit to the ERF as shown in Figure 2. It is easier to integrate the LGF and express the concentration as a function of the deposited thickness. The deposited film layer thickness ($h$) can be obtained from the concentration profile according to eq 11

$$h = 0.59\sigma \ln(1 + e^{(z_i - 0.59\sigma)})$$  \hspace{1cm} (13)

Substituting $z = 0$ in eq 12 gives the expression for the film surface coverage ($\theta$), and rearranging yields

$$1 + e^{(z_i - 0.59\sigma)} = \frac{1}{1 - \theta}$$  \hspace{1cm} (14)

Substituting eq 14 in eq 13 and rearranging yields

$$\theta = 1 - e^{-(h/0.59\sigma)}$$  \hspace{1cm} (15)

Equating eqs 4 and 15 and using eq 7, it is possible to express the effective interface width ($\sigma$) as a function of the surface-energy difference between the layer materials

$$\sigma = \frac{1}{0.59} \left[1 + e^{-(\gamma_f - \gamma_s)/\Delta E}\right]$$

$$\sigma = \frac{1}{0.59} A [1 + e^{-B(\gamma_f - \gamma_s)}]$$  \hspace{1cm} (16)

The values of the effective parameters $A = (N_{sd}^f/N_{sd}^i)$ and $B = \frac{1}{(K_0 T + \Delta E)}$ can be extracted from the experimental dependence of $\sigma$ on $\gamma_f - \gamma_s$. By understanding the relation between the effective parameters and the material properties, it must be possible to calculate the effective interface width for any TM-on-TM system with a given surface-energy difference ($\gamma_f - \gamma_s$).

### 2.3. Surface Energy Values

Several theoretical calculations have been performed in the last decades to determine the crystal facet-dependent surface energy values.\textsuperscript{30,31} In contrast, experimental surface-energy values for solid metals are usually obtained from the surface tension measurements of metals in the liquid phase.\textsuperscript{32} These surface-energy values are independent of surface orientation and thus correspond to an averaged crystal plane orientation. Sputter-deposited thin films are usually amorphous for the first few deposited monolayers, after which a polycrystalline growth with different surface facets is observed. Thus, the facet-independent experimental surface-energy values are more relevant to sputter-deposited films than the calculated facet-dependent values. For this reason, values of surface energies ($\Delta f$/m$^2$) for solids obtained from surface tension measurements compiled by de Boer et al.\textsuperscript{21} are used in this work. The surface energy per atom ($\Delta f$/atom) can be calculated from the surface energy per unit area ($\Delta f$/m$^2$) when the effective molar surface area ($S_m$) is known. The surface area of an atom is calculated from the molar volume ($V_m$) by assuming a certain shape for the atomic cell. For instance, the surface area ($S$) of a spherical atomic cell is given by

$$S = 4\pi \left(\frac{V_m}{N_0}\right)^{2/3}$$  \hspace{1cm} (17)

where $N_0$ is the Avogadro’s number. However, only a fraction ($f$) of the surface area of a surface atom contributes to the effective surface area that is exposed to vacuum. The value of $f$ depends on the number of nearest neighbors of an atom. As it is not trivial to express $f$ as a function of coverage, we assume that effectively, one-third of the surface area of the spherical atomic cell is exposed to vacuum. The effective surface area of a mole of surface atoms ($S_m$) is then given by the equation

![Figure 2. Comparison between an ERF curve according to eq 10 and an LGF curve according to eq 12. The values of $z_i$ and $\sigma$ are 5 and 1, respectively. The absolute error between the curves is shown in the bottom plot.](image-url)
The surface energy values used in this work are listed in Table 1.

Table 1. List of Surface Energy Values

| TM    | crystal structure at normal temperature and pressure | surface energy from de Boer et al.\(^a\) (J/m\(^2\)) | effective molar surface area, \(S_m \times 10^3\) (m\(^2\)/mol) | surface energy (eV/atom) |
|-------|----------------------------------------------------|---------------------------------------------------|-------------------------------------------------|--------------------------|
| Sc    | hcp                                                | 1.28                                              | 8.22                                            | 1.09                     |
| Ti    | hcp                                                | 2.10                                              | 6.54                                            | 1.42                     |
| V     | bcc                                                | 2.55                                              | 3.75                                            | 1.52                     |
| Cr    | bcc                                                | 2.30                                              | 5.05                                            | 1.20                     |
| Mn    | bcc                                                | 1.60                                              | 5.13                                            | 0.85                     |
| Fe    | bcc                                                | 2.48                                              | 4.99                                            | 1.28                     |
| Co    | hcp                                                | 2.55                                              | 4.80                                            | 1.27                     |
| Ni    | fcc                                                | 2.45                                              | 4.75                                            | 1.21                     |
| Cu    | fcc                                                | 1.83                                              | 4.99                                            | 0.94                     |
| Zn    | hcp                                                | 0.99                                              | 5.93                                            | 0.61                     |
| Y     | hcp                                                | 1.13                                              | 9.89                                            | 1.15                     |
| Zr    | hcp                                                | 2.00                                              | 7.89                                            | 1.63                     |
| Nb    | bcc                                                | 2.70                                              | 6.63                                            | 1.85                     |
| Mo    | bcc                                                | 3.00                                              | 6.02                                            | 1.87                     |
| Tc    | hcp                                                | 3.15                                              | 5.63                                            | 1.84                     |
| Ru    | hcp                                                | 3.05                                              | 5.54                                            | 1.75                     |
| Rh    | fcc                                                | 2.70                                              | 5.54                                            | 1.55                     |
| Pd    | fcc                                                | 2.05                                              | 5.80                                            | 1.23                     |
| Ag    | fcc                                                | 1.25                                              | 6.40                                            | 0.83                     |
| Cd    | hcp                                                | 0.74                                              | 7.51                                            | 0.58                     |
| La    | hcp                                                | 1.02                                              | 10.2                                            | 1.08                     |
| Hf    | hcp                                                | 2.15                                              | 7.70                                            | 1.71                     |
| Ta    | bcc                                                | 3.15                                              | 6.64                                            | 2.17                     |
| W     | bcc                                                | 3.68                                              | 6.07                                            | 2.31                     |
| Re    | hcp                                                | 3.60                                              | 5.78                                            | 2.16                     |
| Os    | hcp                                                | 3.45                                              | 5.62                                            | 2.01                     |
| Ir    | fcc                                                | 3.00                                              | 5.65                                            | 1.75                     |
| Pt    | fcc                                                | 2.48                                              | 5.89                                            | 1.51                     |
| Au    | fcc                                                | 1.50                                              | 6.36                                            | 0.99                     |

3. EXPERIMENT AND METHODOLOGY

TM-on-TM bilayer systems were deposited in an ultrahigh vacuum sputter deposition chamber with in vacuo transfer to an IONTOF QtaC\(^{100}\) HS-LEIS set up. Grazing incidence X-ray reflectivity (GIXRR) measurements were performed using a PANalytical Empyrean X-ray diffractometer (Cu K\(\alpha\): 0.154 nm). A Bruker Dimension Edge atomic force microscope with high-resolution tip (MikroMasch HiRes-C15/Cr-Au) was used for surface morphology characterization.

3.1. Deposition. All samples were deposited using dc magnetron sputtering with krypton as the sputter gas in a deposition chamber with <5 \times 10^{-9} mbar base pressure and 1 \times 10^{-3} mbar working pressure. The substrate-to-target distance was 8 cm. Single-side polished Si(100) wafers with \(\sim 1\) nm native oxide and 0.15 \pm 0.05 nm root-mean-square (rms) roughness were used as substrates for deposition. The sputter voltage for the materials used was in the range of 300–600 V; so similar particle energies can be expected for all depositions. Each magnetron had a shutter in front to prevent cross-contamination and a quartz crystal microbalance at close proximity to monitor the deposition rate and thickness. The deposition rates were calibrated by means of ex-situ GIXRR measurements on thick reference samples.

A bilayer architecture as shown in Figure 3 was used for all TM-on-TM systems studied in this work. A 4 nm-substrate layer was deposited directly on the Si wafer with native oxide, and the film layer is grown on top. It is well known that thin metal layers grown on SiO\(_2\) tend to dewet and form islands at high temperatures.\(^{33,34}\) Therefore, the native oxide is generally removed from the Si wafer prior to deposition. Since all experiments presented in this work were carried out near room temperature, it was beneficial not to remove the native oxide, as its presence can reduce the intermixing between the substrate layer and the Si wafer.\(^2\) To evaluate the effect of substrate layer morphology on film layer growth, the 4 nm-substrate layers were studied using atomic force microscopy (AFM). The rms roughness values are presented in Table 2. All materials except Cu show rms roughness in the range of \(\sim 0.2\) nm, which represents a typical smooth substrate layer growth. The Cu substrate layer shows higher roughness by a factor 3, but no island formation was observed. Therefore, morphology of the substrate layers is expected to have no influence on the film layer growth.

3.2. HS-LEIS. In the LEIS technique, a noble gas primary ion with 1–8 keV energy is directed toward the sample surface at a fixed incidence angle. The energy of the backscattered ion provides information about the mass of the scattering surface atom according to the laws of conservation of energy and conservation of momentum. The advantage of HS-LEIS over conventional LEIS is the high LEIS signal-to-primary ion current ratio.\(^35\) This allows us to use a low primary ion current and, therefore, reduce the primary ion-induced damage to the sample surface during LEIS measurement. HS-LEIS coupled with the in vacuo sample transfer provides the possibility to measure the surface composition of as-deposited unaltered surfaces. More information about the LEIS technique can be found in ref 36.

In this work, HS-LEIS measurements were performed using an IONTOF QtaC\(^{100}\) tool with 1 \times 10^{-12} mbar base pressure. A 5 keV Ne\(^+\) primary ion beam with 1 nA current at normal incidence was used for the LEIS measurements. There are two main benefits of using Ne\(^+\) primary ion instead of He\(^+\): (1) it has higher mass resolution and (2) the effect of the background signal from a heavier element on the surface peak of a lighter element is reduced. An Ar\(^+\) sputter gun operating at 0.5 keV ion energy and 59° incidence angle relative to the surface normal was used for the sputter depth profile measurements.
3.3. LEIS Growth Profile. Sputter depth profile measurement often induces strong intermixing of the layers under investigation. To avoid this, we use a nondestructive method called LEIS growth profile. The procedure for recording a growth profile is described below with Mo-on-Pt as an example system. The same methodology was used for all other TM-on-TM systems presented in this work.

(1) 4 nm Pt layer was deposited on the Si wafer followed by 0.3 nm of Mo layer
(2) Sample was transferred in vacuo to the LEIS chamber, and LEIS spectrum was collected using Ne+ primary ions
(3) 4 nm Pt layer was deposited on a new Si wafer followed by the Mo layer with a sub-nanometer increase in the thickness
(4) Steps 2 and 3 were repeated until the Mo layer signal saturates, which corresponds to 100% Mo film layer coverage

Typical LEIS spectra of Mo-on-Pt are shown in Figure 4a. The LEIS surface peaks that correspond to Mo and Pt are labelled in the figure. The integral area of the surface peaks is a direct measure of the number of Mo and Pt atoms present on the surface. The surface coverage of Mo and Pt for each growth step can be calculated from the ratio of integral peak areas of the investigated sample and the respective reference layers. The surface coverage evolution as a function of the as-deposited film thickness (Figure 4b) can be used to obtain the effective interface width and to reconstruct the in-depth profile. Because LEIS cannot differentiate between intermixing and island formation, it is important to evaluate the surface morphology of the deposited film layer using an ex situ atomic force microscope. Additionally, LEIS sputter depth profile is performed at various film thicknesses to qualitatively check if the evolution of the surface coverage is influenced by surface segregation effects.

4. RESULTS AND DISCUSSION

4.1. Growth Profile Types of TM-on-TM Systems. According to the proposed surface-exchange model, the evolution of the film coverage as a function of the as-deposited film layer thickness is directly related to the intermixing process during growth, and hence, the LEIS growth profile can be defined by a simple LGF-like interface model. We observe
Table 3. Overview of All Investigated TM-on-TM Systems Exhibiting Type-I Growth Profile and the Corresponding Surface-Energy Difference ($\gamma_s - \gamma_f$), Effective Interface Width ($\sigma$), and rms Roughness Values

| TM-on-TM | $\gamma_s - \gamma_f$ (eV/atom) | $\sigma$ (nm) | rms roughness ± 0.05 nm |
|----------|-------------------------------|--------------|------------------------|
| Mo-on-Nb | -0.02                         | 0.37 ± 0.04  | 0.16                   |
| Nb-on-Mo | 0.02                          | 0.25 ± 0.04  | 0.17 (0.6 nm Nb-on-Mo) |
| Ru-on-W  | 0.56                          | 0.36 ± 0.02  | 0.21                   |
| W-on-Ru  | -0.56                         | 0.75 ± 0.01  | 0.21                   |
| W-on-Ti  | -0.89                         | 1.00 ± 0.01  | 0.16                   |
| Ti-on-W  | 0.89                          | 0.39 ± 0.02  | 0.16                   |
| Pd-on-W  | 1.08                          | 0.38 ± 0.02  | 0.16                   |
| W-on-Pd  | -1.08                         | 1.65 ± 0.03  | 0.16                   |
| Cr-on-W  | 1.11                          | 0.23 ± 0.01  | 0.18                   |
| W-on-Cr  | -1.11                         | 0.69 ± 0.02  | 0.18                   |
| Pt-on-Ta | 0.66                          | 0.64 ± 0.06  | 0.14 (1.5 nm Pt-on-Ta) |
| Ta-on-Pt | -0.66                         | 1.03 ± 0.09  | 0.19 (1.5 nm Ta-on-Pt) |
| Mo-on-Ta | 0.30                          | 0.40 ± 0.02  | 0.17                   |
| Ta-on-Mo | -0.30                         | 0.36 ± 0.02  | 0.17                   |
| Mo-on-Pt | -0.36                         | 0.77 ± 0.02  | 0.43                   |
| Pt-on-Mo | 0.36                          | 0.48 ± 0.03  | 0.17                   |
| Ru-on-Pt | -0.24                         | 0.98 ± 0.03  | 0.18                   |
| Pt-on-Ru | 0.24                          | 0.72 ± 0.02  | 0.19 (1.5 nm Pt-on-Ru) |
| Zr-on-Ta | 0.53                          | 0.41 ± 0.02  | 0.19                   |
| Zr-on-Pt | -0.12                         | 1.12 ± 0.03  | 0.19 (1.2 nm Zr-on-Pt) |
| Mo-on-Zr | 0.24                          | 0.51 ± 0.06  | 0.12                   |

*The rms roughness values are obtained from the AFM measurements of 0.9 nm TM-on-(4 nm) TM samples, and the exceptions are mentioned within the brackets.*

An LGF-like interface model (eq 15) clearly cannot describe the surface coverage evolution of the film atoms. Recently, Zameshin has developed a model that separates intermixing and segregation phenomena in the growth of Ru films on Si, B, C, and B,C layers. According to this model, additional segregation of substrate atoms during layer growth is purely a surface effect (“floating segregation”) that does not affect the subsurface composition. We consider that the floating substrate atoms are removed from the surface only via defect sites or grain boundaries as subsequent layers are being deposited. As a result, the floating segregation of substrate atoms affects only the surface coverage during growth, whereas the in-depth LGF-like interface profile is not affected significantly. The surface coverage of the film layer according to Zameshin’s segregation model is

$$C(z = 0, h, \alpha, \lambda) = \theta(h, \alpha, \lambda) = \left(1 - e^{-h/(0.59\sigma)}\right) - \left(\alpha \frac{1}{0.59\sigma\lambda} (e^{-2h/0.59\sigma} - e^{-h})\right)$$ (19)

The dimensionless parameter $\alpha$ can be called the strength of floating segregation of substrate atoms as it indicates the addition of newly segregated atoms during growth. The parameter $\lambda$, with an inverse length unit, denotes the effectiveness of removal of the segregated atoms. In the simplest case of no floating segregation ($\alpha = 0$), the model simplifies to type-I growth. The effective interface width ($\sigma$) and the segregation parameters ($\alpha$ and $\lambda$) for type-II TM-on-TM systems can be obtained by fitting the growth profile according to eq 19. We use the following constraints while fitting to obtain a physically realistic profile and reasonable values for the fit parameters: the rate of increase of film

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that this is true for most of the investigated TM-on-TM systems. However, in some systems, an LGF-like interface model cannot fully describe the LEIS growth profile. We will show that in these cases, the LEIS growth profile can be explained by considering contributions from the surface segregation of the substrate or film atoms to the growth profile in addition to the intermixing process. The definition of surface segregation in our work is tailored for the surface composition changes during thin-film growth. We define it as the enrichment of the surface by the film or substrate atoms during growth in comparison to the surface composition due to the intermixing process described by Ex-1 and Ex-2 mechanisms. Further details are discussed later in this section. We categorize all TM-on-TM systems studied in this work into one of the following growth profile types based on the observed intermixing and segregation characteristics:

1. **Type-I growth profile:** only intermixing process and no segregation of film or substrate atoms
2. **Type-II growth profile:** segregation of substrate atoms in addition to the intermixing process
3. **Type-III growth profile:** segregation of film atoms in addition to the intermixing process
4. **Type-IV growth profile:** strong segregation of substrate atoms in addition to the intermixing process

We will first explain each growth profile type with example systems followed by the overall discussion at the end of the section.

Type-I growth profile, the most commonly observed growth type, is exhibited by TM-on-TM systems in which the evolution of surface coverage as a function of as-deposited film layer thickness is defined purely by the surface-exchange processes (Ex-1 and Ex-2) during growth according to eq 4. LEIS growth profiles of Zr-on-Pt and Zr-on-Ta, representatives of type-I growth profile, are shown in Figure 5. The effective interface width ($\sigma$) can be obtained by fitting the growth profile using an LGF-like interface model given by eq 15. AFM images (not presented here) show a 2D growth with rms surface roughness value in the range of 0.2 nm. This means that the evolution of film layer coverage is a direct effect of intermixing during growth and not due to island formation.

An overview of all investigated TM-on-TM systems exhibiting type-I growth profile is presented in Table 3. An asymmetry in the interfaces between two materials, as previously observed in the Cr/Sc multilayer, can be seen in the investigated TM-on-TM systems. For example, the W-on-Pd interface width is 4 times larger than the Pd-on-W interface width. In general, this phenomenon can be explained by the surface-energy difference between the film and substrate atoms. When the surface energy of the substrate atom is lower than that of the film atom, the probability of Ex-2 during growth increases, resulting in a wide interface. In contrast, the interface width is comparatively sharper when the film atom surface energy is lower than that of the substrate atom.

LEIS growth profiles of Pt-on-Zr and Co-on-Hf, representatives of type-II growth profile, are shown in Figure 6. Type-II growth profile is exhibited by TM-on-TM systems in which there is an additional drive, besides Ex-1 and Ex-2, for substrate atoms to move to the surface. Additional segregation of substrate atoms to the surface results in higher surface coverage of substrate atoms (lower surface coverage of film atoms) than what it should have been with only Ex-1 and Ex-2 processes. The LEIS growth profile fit (Figure 6a,c) based on
coverage is always positive ($d\theta/dh \geq 0$) and the film coverage is between $0$ and $1$ ($0 \leq \theta \leq 1$).

Type-II growth profiles fitted using Zameshin’s model are shown in Figure 6b,d. Zameshin’s model, with corresponding contributions from the film coverage in the absence of floating segregation (first term in eq 19, dotted line) and the floating substrate atoms (second term in eq 19, dashed line), explains the growth profile better than the standard LGF-like interface model. The coverage of floating substrate atoms increases initially as more film atoms arrive at the surface of the pure substrate layer. The segregated atom coverage reaches a maximum as all exchange sites are covered and further segregation of substrate atoms from the buried substrate layer is strongly hindered. Some of the floating substrate atoms segregate further as subsequent atoms are deposited, whereas the rest are removed via defect sites or grain boundaries without significantly impacting the in-depth concentration of the film atoms. This results in a decrease in the coverage of the floating substrate atoms as a function of the as-deposited film thickness, and it eventually reaches zero when there are no more floating atoms.

An overview of all investigated TM-on-TM systems exhibiting type-II growth profile and the corresponding surface-energy difference ($\gamma_s - \gamma_f$), Zameshin’s Segregation Model Parameters ($\alpha$ and $\lambda$), Effective Interface Width ($\sigma$), and rms Roughness Values$^a$

| TM-on-TM   | $\gamma_s - \gamma_f$ (eV/atom) | $\alpha$ | $\lambda$ (nm$^{-1}$) | $\sigma$ (nm) | rms roughness ($\pm$0.05 nm) |
|------------|---------------------------------|---------|------------------------|---------------|-----------------------------|
| Mo-on-Zr   | -0.24                           | 0.98$^{\pm0.02}$ | 2.8$^{\pm0.8}$          | 0.7$^{\pm0.1}$ | 0.48                        |
| Pt-on-Zr   | 0.12                            | 0.79$^{\pm0.06}$ | 1.9$^{\pm0.1}$          | 1.02$^{\pm0.09}$ | 0.15                        |
| Co-on-Hf   | 0.45                            | 1.02$^{\pm0.08}$ | 2.7$^{\pm0.6}$          | 0.81$^{\pm0.08}$ | 0.14                        |
| Pd-on-Cu   | -0.29                           | 0.36$^{\pm0.08}$ | 1.2$^{\pm0.4}$          | 1.6$^{\pm0.2}$ | 0.42                        |
| Pt-on-Cu   | -0.57                           | 0.8$^{\pm0.08}$  | 1.0$^{\pm0.1}$          | 1.9$^{\pm0.2}$ | 0.36                        |

$^a$The rms roughness values are obtained from the AFM measurements of 0.9 nm TM-on-(4 nm) TM samples.

Figure 6. Representatives of type-II growth profile: LEIS growth profile of Pt-on-Zr with the (a) LGF-like interface model fit and (b) Zameshin’s segregation model fit, and LEIS growth profile of Co-on-Hf with the (c) LGF-like interface model fit and (d) Zameshin’s segregation model fit.

Table 4. Overview of All Investigated TM-on-TM Systems Exhibiting Type-II Growth Profile and the Corresponding Surface-Energy Difference ($\gamma_s - \gamma_f$), Zameshin’s Segregation Model Parameters ($\alpha$ and $\lambda$), Effective Interface Width ($\sigma$), and rms Roughness Values$^a$
when a system shows type-II growth profile, it does not automatically make the inverse system also type-II. For instance, Mo-on-Zr and Pt-on-Zr show type-II growth profile, whereas Zr-on-Mo and Zr-on-Pt show type-I growth. Nevertheless, the asymmetry in the interface width is still valid and can be explained by the surface-energy difference.

LEIS growth profiles of Cu-on-Pt and Hf-on-Co, representatives of type-III growth profile, are shown in Figure 7. Type-III growth profile is exhibited by TM-on-TM systems in which there is an additional drive for film atoms to stay on the surface, which is the exact opposite of type-II growth where the substrate atoms float on the surface. LEIS growth profile fit (Figure 7a,c) based on an LGF-like interface model (eq 15) once again cannot describe the surface coverage evolution of the film atoms. Also, Zameshin’s segregation model is derived for the segregation of substrate atoms during growth and not for film atoms. Currently, we do not have a model to describe the floating segregation of film atoms. For this reason, we use Zameshin’s model with a negative \( \alpha \) to represent the reverse segregation of substrate atoms, in other words, segregation of film atoms. The effective interface width (\( \sigma \)) and the segregation parameters (\( \alpha \) and \( \lambda \)) for type-III TM-on-TM systems are obtained by fitting the growth profile using Zameshin’s model according to eq 19.

Type-III growth profiles fitted using Zameshin’s model are shown in Figure 7b,d. Zameshin’s model with a negative \( \alpha \) describes the observed growth profile data well. The floating segregation of film atoms increases in the initial stages of growth and eventually goes to zero similar to the type-II growth. However, the effectiveness of removal of the segregated atoms is significantly greater in type-III growth, which can be explained by the fact that the film and segregating atoms are the same element.

An overview of all investigated TM-on-TM systems exhibiting type-III growth profile is presented in Table 5. A correlation is observed between the parameters \( \alpha \) and \( \lambda \), which allows for a wide range of possible solutions. The values of \( \alpha \) and \( \lambda \) are obtained from the fitting of the growth profiles using Zameshin’s model.

### Table 5. Overview of All Investigated TM-on-TM Systems Exhibiting Type-III Growth Profile and the Corresponding Surface-Energy Difference (\( \gamma_s - \gamma_f \)), Zameshin’s Segregation Model Parameters (\( \alpha \) and \( \lambda \)), Effective Interface Width (\( \sigma \)), and rms Roughness Values

| TM-on-TM | \( \gamma_s - \gamma_f \) (eV/atom) | \( \alpha \) | \( \lambda \) (nm\(^{-1}\)) | \( \sigma \) (nm) | rms roughness (±0.05 nm) |
|----------|----------------------------------|----------|----------------|--------------|--------------------------|
| Sc-on-Ru | 0.66                             | −1.94    | 16.51          | 0.64\(^{0.05}_{0.00}\) | 0.16                     |
| Sc-on-Cu | −0.14                            | −11.99   | 28.19          | 1.12\(^{0.09}_{0.08}\) | 0.94                     |
| Sc-on-Ir | 0.67                             | −5.13    | 18.13          | 0.69\(^{0.01}_{0.01}\) | 0.14                     |
| Hf-on-Co | −0.45                            | −11.42   | 35.80          | 1.26\(^{0.09}_{0.07}\) | 0.18                     |
| Cu-on-Cr | 0.26                             | −1.96    | 18.02          | 0.60\(^{0.05}_{0.05}\) | 0.25                     |
| Cu-on-W  | 1.37                             | −5.23    | 24.01          | 0.46\(^{0.05}_{0.07}\) | 0.58                     |
| Cu-on-Ru | 0.81                             | −7.24    | 47.64          | 0.71\(^{0.05}_{0.05}\) | 0.16                     |
| Cu-on-Pd | 0.29                             | −4.99    | 25.18          | 1.02\(^{0.10}_{0.05}\) | 0.17                     |
| Cu-on-Pt | 0.57                             | −5.29    | 12.48          | 0.90\(^{0.07}_{0.07}\) | 0.22                     |

*The rms roughness values are obtained from the AFM measurements of 0.9 nm TM-on-(4 nm) TM samples.*
and $\lambda$ given in Table 5 are just an example from the several possible solutions. The effective interface width ($\sigma$) is, however, not affected by the correlation between $\alpha$ and $\lambda$, and hence, the mean and the uncertainty values of $\sigma$ obtained from the fits are reliable. It is important to note that the floating segregation of film atoms in type-III systems occurs even when the substrate atom surface energy is lower than that of the film atoms as observed for Hf-on-Co and Sc-on-Cu. Similar to the case of type-II systems, another energy term besides surface energy is expected to influence the segregation.

![Figure 8](image1.png)

**Figure 8.** Representatives of type-IV growth profile: LEIS growth profile of Ru-on-Sc with the LGF-like interface model fit and (b) LEIS growth profile of Ta-on-Zr with the LGF-like interface model fit.

![Figure 9](image2.png)

**Figure 9.** (a) Schematic representation of the intermixed interface exhibited by type-I, type-II, and type-III systems and (b) LEIS sputter profile of 1.2 nm Zr-on-Ta. (c) Schematic representation of strong floating segregation of substrate atoms in addition to an intermixed interface exhibited by type-IV systems and (d) LEIS sputter profile of 5.4 nm Ta-on-Zr.
process in type-III systems. Finally, surface roughness does not seem to have a strong influence on type-III growth also.

LEIS growth profiles of Ru-on-Sc and Ta-on-Zr, representatives of type-IV growth profile, are shown in Figure 8. Type-IV growth profile is exhibited by TM-on-TM systems in which there is an additional drive for substrate atoms to segregate to the surface as in the case of type-II systems but with a much stronger effect of floating segregation. At first glance, the fit based on the LGF-like interface model (eq 15) seems to describe the type-IV growth profile reasonably well. However, the LEIS sputter profiles showed a surprising observation in contrast to what was observed for type-I, -II, and -III systems. When the samples were sputtered, the substrate atom coverage decreased substantially, whereas the film atom coverage increased by a similar magnitude. Later, it will be shown that this effect can be explained only by strong floating segregation of substrate atoms. The fit obtained using the LGF-like interface model is therefore not valid. Moreover, a unique fit using Zameshin’s segregation model is also not possible because of a strong correlation among the model parameters as a result of strong floating segregation.29 Hence, it is not possible to obtain a reliable value for the effective interface width from the LEIS growth profiles of type-IV systems.

It should be emphasized that strong floating segregation does not actually mean a large effective interface width, as suggested by the growth profile (Figure 8). The floating segregation in type-IV systems can still be considered a surface effect as in the case of type-II systems. The main difference between type-II and type-IV systems is that the floating segregation of substrate atoms in type-II is removed within the intermixed zone, whereas in type-IV, the effect of floating segregation continues further into the film layer. The effective interface width due to intermixing in type-IV systems is, however, expected to remain unaffected by the floating segregation, although it cannot be directly extracted from the LEIS growth profiles.

The schematic representations and the LEIS sputter profiles of an intermixed interface with no or limited segregation (type-I, type-II, and type-III systems) and an intermixed interface with strong floating segregation of substrate atoms (type-IV systems) are shown in Figure 9. The LEIS sputter depth of 1.2 nm Zr-on-Ta (Figure 9b), representative of an intermixed interface, clearly shows the expected decrease in film (Zr) coverage and increase in substrate (Ta) coverage as a function of Ar sputter ion fluence. The coverage of Zr eventually reaches 0% (and 100% for Ta) as we sputter away the intermixed zone completely and enter the Ta substrate layer. The LEIS sputter profile of the inverse system, 5.4 nm Ta-on-Zr, representative of an intermixed interface with strong floating segregation of substrate atoms, is shown in Figure 9d. The film (Ta) coverage increases initially as the floating substrate (Zr) atoms are sputtered away. The growth of a pure film (Ta) layer under the floating substrate (Zr) atoms is evident from the LEIS sputter profile. As we sputter away the pure Ta film layer completely and enter the intermixed zone, the Ta coverage starts to decrease, whereas Zr coverage increases.

Apart from the cases with strong floating segregation of substrate atoms, type-IV growth profile also includes cases where island formation affects the growth profile, though island formation during growth alters the intermixing process such that an LGF-like interface profile is no longer valid. LEIS growth profile and AFM images of W-on-Cu, representative of type-IV growth profile with island formation, are shown in Figure 10. The surface coverage of W increases initially from 0 to 10% for 0.3 nm W-on-Cu for which a 2D growth mode is observed. The growth changes to a 3D island mode at 0.6 nm W-on-Cu. This change in growth mode from 2D to 3D with an increment of 0.3 nm shows the high surface mobility even near
room temperature. Further increase in the W thickness results in an increase in both island density and height of each island, whereas the surface coverage of W (and Cu) remains unchanged, indicating a strong floating segregation of Cu in the islands. Ultimately, around 3.3 nm W-on-Cu, the growth changes back to 2D growth as the islands coalesce together. After this point, the surface coverage of W starts to increase (and Cu coverage decreases) because of the removal of floating Cu atoms via defect sites or grain boundaries. LEIS sputter profile of 7.8 nm W-on-Cu sample showed an increase in the W surface coverage from 76 to 100%, which means that the pure W film layer growth begins around this point.

An overview of all investigated TM-on-TM systems exhibiting type-IV growth profile is presented in Table 6. It is not possible to extract reliable values for the interface parameters ($\sigma$, $\alpha$, and $\lambda$) from the LEIS growth profiles of type-IV systems because of strong floating segregation. The inverse combinations of all type-IV systems show either type-I or type-III growth. For instance, Ta-on-Zr shows type-IV growth, whereas Zr-on-Ta shows type-I growth.

As shown earlier, surface energy is not the only driving factor for floating segregation as it occurs even when the surface energy of the floating atom is not favorable for segregation. Surface roughness also does not seem to contribute to floating segregation, although 3D growth can alter the intermixing process. Because all investigated materials were sputter deposited under similar conditions, it is unlikely that the deposition process affects the floating segregation of atoms during growth. The only noticeable connection between floating segregation in type-II, type-III, and type-IV systems is the elements that tend to segregate to the surface. Out of all 15 investigated TMs, only Zr, Hf, Sc, and Cu show floating segregation behavior. In terms of the atomic size (metallic radius), Sc, Zr, and Hf are the largest, whereas Co, Cu, and Cr are the smallest among the TMs studied in this work. The large size difference between the film and substrate atoms can induce strain during intermixing. Because we do not consider strain energy in the surface-exchange model, we are unable to provide a quantitative analysis for the floating segregation observed during growth. Also, it is possible that the strain energy on the surface, especially during growth, is different from that of the bulk. Nevertheless, the effect of size difference on growth types can still be considered qualitatively.

The difference in atomic radii between the substrate and film atoms ($r_s - r_f$) for all investigated TM-on-TM systems is shown in Figure 11. The difference in atomic radii of all type-I systems is mostly close to zero, which explains why the size-related effects in type-I growth are negligible. For type-II systems, we observe two cases: (i) systems with a large positive atomic radii difference, where the substrate atom is much larger than the film atom and (ii) systems with a size difference comparable to type-I systems. For type-III systems, we observe two cases: (i) systems with a large negative atomic radii difference, where the substrate atom is much larger than the film atom and (ii) systems with a size difference comparable to type-I systems.

In type-II and type-IV systems, for a large positive atomic radii difference (case i), the largest atom (Hf, Zr, and Sc in our case) always tends to float on the surface, consequently reducing the strain energy in the surface layer. It is important to note that although Co-on-Hf and Cu-on-Sc have the same atomic radii difference, they exhibit different growth profile types, type-II and type-IV, respectively. This can be explained by the surface-energy difference between Co–Hf (0.45 eV/...
Table 7. Empirical Rules To Predict the Probable Growth Profile Type in TM-on-TM Systems Based on the Atomic Radii Difference (\(r_i - r_j\)), Enthalpy of Mixing, and Surface-Energy Difference

| system       | \(r_i - r_j\) (Å) | enthalpy of mixing (kJ/mol) | probable growth profile type | element expected to segregate |
|--------------|-------------------|----------------------------|----------------------------|-----------------------------|
| TM-on-TM     | −0.22 to +0.12     | + or −                      | type-I                     | substrate                   |
|              | >+0.12             | −                           | type-II or type-IV (depending on surface-energy difference and size difference) | substrate                   |
|              | <−0.22             | + or −                      | type-IV                    | substrate                   |
| Cu\(^{++}\)-on-TM | −0.22 to +0.12 | + or −                      | type-III                   | Cu                          |
|              | >+0.12             | −                           | type-II or type-IV (depending on surface-energy difference and size difference) | substrate                   |
| TM-on-Cu\(^{++}\) | −0.22 to +0.12 | + or −                      | type-III                   | Cu                          |

\(\text{Ag and Au may show similar behavior as Cu because of their low melting point.}\)

atom) and Cu−Sc (0.14 eV/atom). In Co-on-Hf, the large size difference drives the floating segregation of the substrate Hf atom, but the low surface energy of the Co film atom limits the floating segregation, resulting in a type-II growth profile. For Cu-on-Sc, the large size difference drives the floating segregation of the substrate Sc atom, and the small difference in surface energy does not hinder the floating segregation, resulting in a type-IV growth profile. In effect, the interplay between the surface-energy difference and the atomic size difference determines if a TM-on-TM system exhibits type-II or type-IV growth profile. Similarly, in type-III systems, for a large negative atomic radii difference (case i), the largest atom (Hf and Sc in our case) tends to float. Note that Zr-on-Ta, Zr-on-Mo, and Zr-on-Pt have larger negative atomic radii difference, when compared to other type-I systems and may exhibit floating segregation of Zr in the initial stages of growth. However, the effect is not significant enough to affect the growth at a film thickness of 0.3 nm or later. This is why these systems show a typical type-I growth profile.

All case (ii) TM-on-TM systems in type-II and type-III have Cu as the element that exhibits floating segregation. The atomic size difference in these systems is comparable to type-I systems and hence does not seem to play an important role. The magnitude of segregation is, however, influenced by the surface-energy difference. For example, floating segregation of Cu in Pt-on-Cu is stronger than in Pd-on-Cu because of larger negative surface-energy difference (Table 4). Interestingly, in Sc-on-Cu and Cu-on-Sc, Sc is the element that exhibits floating segregation. This means Cu tends to float on the surface in Cu-on-TM and TM-on-Cu systems, provided the TM is not a large atom like Sc, where size effects dominate. It is not clear what drives the floating segregation of Cu during layer growth. The low melting point of Cu (the lowest of all TMs studied in this work) suggests a low activation energy for self-diffusion, which can possibly explain its preference to float on the surface. The effect of high surface mobility can also be seen in W-on-Cu where the growth changes from 2D to 3D with an increment of 0.3 nm W thickness (Figure 10). This means, other TMs with a low melting point such as Ag and Au can also be expected to show floating segregation behavior. Nevertheless, further work is required to understand the floating behavior of Cu in detail.

The case (ii) TM-on-TM systems in type-IV show no size dependence either. A unique relation among these systems is that they all have a positive enthalpy of mixing: Cu−Cr (+12.39 kJ/mol), Zr−Ta (+2.74 kJ/mol), Cu−W (+22.33 kJ/mol), and Cu−Ru (+6.98 kJ/mol). All other investigated TM-on-TM systems have a negative enthalpy of mixing, \(^{19,22}\) with one exception: W−Cr has a positive enthalpy of mixing (+0.95 kJ/mol), but both W-on-Cr and Cr-on-W show type-I growth profile. On this basis, it is possible to conclude that the positive enthalpy of mixing seems to affect only those TM-on-TM systems with substrate atoms that tend to float. W-on-Cu, Ru-on-Cu, and Cr-on-Cu are expected to show a type-II growth profile (floating segregation of substrate atoms) like Pd-on-Cu and Pt-on-Cu, but the positive mixing energy drives the floating segregation of Cu to a larger extent such that it becomes type-IV growth profile with Cu atoms floating beyond the intermixed zone. This explanation is valid for Ta-on-Zr system also. The inverse systems Zr-on-Ta, Cu-on-W, Cu-on-Ru, and Cu-on-Cr, where the film atom exhibits floating segregation, are not affected by the positive mixing enthalpy. Cr and Cu are similar in size, and still Cr does not show floating behavior in W-on-Cr and Cr-on-W systems even when there is a positive mixing energy. This suggests that the floating behavior of Cu is its inherent property and is not due to its small atomic radius. Large positive mixing enthalpy of W−Cu also explains the 3D island growth in the W-on-Cu system. An interplay between surface energy and mixing enthalpy determines if the layer growth will be 2D or 3D.

The layer materials for TM-on-TM growth studies were chosen to have a diverse combination from different groups and periods within the TM block. Therefore, the layer growth results presented here are believed to be of relevance for all TM-on-TM combinations in general. On the basis of current data set, we propose a general rule to predict the growth type of a TM-on-TM system as given in Table 7.

In summary, floating segregation during growth is purely a surface effect, and it does not fundamentally affect the intermixing process or the interface profile. It is caused by the large size difference and influenced by the surface-energy difference and enthalpy of mixing. Weak floating segregation in the case of type-II and type-III systems is limited to the intermixed zone, and the floating atoms are removed via defect sites or grain boundaries before the growth of a pure film layer begins. In type-IV systems, floating segregation is much stronger than in type-II systems, and its effect on the growth profile continues beyond the intermixed zone into the film layer. When the atomic radii difference is large, the largest atom always segregates to the surface. Cu tends to segregate to...
the surface in both TM-on-Cu and Cu-on-TM systems except when TM is a large atom like Sc.

4.2. Scaling Law for Intermixing in TM-on-TM Systems. According to the surface-exchange model and the interface profile model explained in the theoretical background section, the effective interface width (\(\sigma\)) between two TM layers is related to the surface energies of the film and substrate atoms as given by eq 16. The values of parameter A (\(N_{sa} / N_{sd}f\)), which denotes intermixing due to ballistic collision, and parameter B, the inverse of effective thermal energy of surface atoms (\(1 / kT + \Delta E\)), can be extracted from the experimental data. As mentioned in the previous section, both A and B can depend on several crystal structure properties of the film and substrate layers, such as the coordination number, nearest neighbor distance, lattice spacing, atomic packing, and stacking sequence. It is important to note that both amorphous and crystalline materials have been shown to exhibit similar short-range order and nearest neighbor properties.38−40 Therefore, A and B must predominantly depend on the preferred crystal structure of the layer materials, irrespective of the crystallinity (amorphous or crystalline). Hence, we categorize the TM-on-TM systems according to their crystal structure combination and evaluate the values of parameters A and B for different structure combinations. All TMs except mercury (Hg) have one of the following three crystal structures at room temperature: bcc, hcp and fcc. Thus, there are six possible structure combinations for TM-on-TM systems: bcc-bcc, hcp-hcp, fcc-fcc, bcc-hcp, bcc-fcc, and hcp-fcc. Figure 12 shows the effective interface width values of type-I, type-II, and type-III TM-on-TM systems plotted as a function of the surface-energy difference (\(\gamma_s - \gamma_f\)) and grouped according to the structure combinations. Interface width values of each structure combination are fitted independently using eq 16, and the values of parameters A and B obtained from the respective fits are presented in Table 8. The fact that all \(\sigma\) values for a given structure combination, irrespective of the TM-on-TM growth type, can be fitted with a single exponential function signifies that A and B predominantly depend on the crystal structure of the film and substrate layers. This also proves that Zameshin’s segregation model can provide accurate effective interface width values for type-II and type-III systems by separating the intermixing and segregation processes.

A clear correlation is found between parameter A and the structure combination. In general, the bond energies follow the order bcc > hcp > fcc.41 This explains why the value of A is the smallest for bcc-bcc and largest for fcc-fcc. The values of parameter B indicate that the effective thermal energy of surface atoms in the bcc structure is greater than those in hcp

![Figure 12](image-url)

**Figure 12.** Effective interface width of all investigated TM-on-TM systems plotted as a function of difference in the surface energy (\(\gamma_s - \gamma_f\)) and categorized according to the crystal structure combination. The exponential fit for each structure combination is based on eq 16.

**Table 8. Values of Effective Parameters A and B for Each Structure Combination Obtained by Fitting the Experimental Effective Interface Width Data**

| TM-on-TM structure combination | A (nm)   | B (1/eV) |
|-------------------------------|---------|---------|
| bcc-bcc                       | 0.11 ± 0.01 | 0.9 ± 0.2 |
| hcp-hcp                       | 0.29 ± 0.02 | 1.0 ± 0.2 |
| fcc-fcc                       | 0.36 ± 0.01 | 1.3 ± 0.1 |
| bcc-hcp                       | 0.16 ± 0.01 | 1.13 ± 0.07 |
| bcc-fcc                       | 0.18 ± 0.01 | 1.37 ± 0.06 |
| hcp-fcc                       | 0.27 ± 0.02 | 1.3 ± 0.5 |

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and fcc structures. Thus, the dependence of intermixing on the surface energy is stronger in fcc-based structure combinations and weaker in bcc-based combinations. Because the exponential trend is unique for each structure combination, they can be used as a scaling law to predict the intermixing in TM-on-TM systems. The effective interface width of any given TM-on-TM can thus be calculated using eq 16 by substituting the appropriate values for surface energies (Table 1) and parameters $A$ and $B$ (Table 8). By using eq 9 instead of eq 16, it is possible to calculate the film layer thickness that is required to achieve a certain film coverage or the film coverage for a certain as-deposited film thickness. This is useful for applications in which it is important to have a closed film layer to prevent the exposure of the substrate layer. Note that the film coverage will be strongly affected by the floating segregation in type-IV growth where the film layer grows under the floating substrate atoms. In such cases, it is possible to remove the floating substrate atoms by physically sputtering or etching the top surface and obtain a pure film surface as shown in Figure 9d.

Finally, it is important to realize that parameters $A$ and $B$ depend on the total energy contribution from the deposition process such as the energy of the incident film atom, substrate temperature, and ion bombardment. Actual values of the effective interface width can deviate from those predicted by the scaling law if the particle energies are considerably different than those typically encountered in magnetron sputtering. However, the relative trends based on the crystal structure and surface-energy difference are expected to be valid for all TM-on-TM systems deposited under similar conditions. Further understanding on the dependence of $A$ and $B$ on the incident atom energy and substrate temperature will enable the quantitative prediction of the interface characteristics for a wide range of deposition conditions.

5. SUMMARY AND CONCLUSIONS

Intermixing during layer growth in sputter-deposited TM-on-TM systems was studied using HS-LEIS. In vacuo LEIS growth profiles were obtained by measuring the surface coverage of film atoms as a function of increasing film layer thickness. The effective interface width values were extracted from the LEIS growth profile fit based on an LGF-like interface profile model. Segregation of substrate or film atoms to the surface (floating segregation) in addition to the standard intermixing process was observed in several TM-on-TM systems. A segregation model developed by Zameshin et al. that separates the intermixing and segregation effects was used to extract the interface width values for such systems. In some TM-on-TM systems, the drive for floating segregation was much stronger, and it was not possible to extract the interface width values by fitting the LEIS growth profile. Overall, we were able to categorize all investigated TM-on-TM systems into four different growth profile types based on the type and strength of segregation observed. Finally, we confirm the exponential dependence of effective interface width on the surface-energy difference according to the proposed surface-exchange model and show that there is a subtrend for each crystal structure combination of TM-on-TM systems. The model parameters extracted from the experimental data can be used to calculate the effective interface width for any TM-on-TM system.

The following conclusions are derived:

1. Intermixing in TM-on-TM systems can be described by the following surface exchange mechanisms: deposition-induced exchange (Ex-1) and surface energy minimization-induced exchange (Ex-2). The effective interface width can be obtained based on an LGF-like interface model. The interface width is large when the surface energy of the substrate atom is lower than that of the film atoms and comparatively sharper for the reverse situation.

2. A large size difference between the film and substrate atoms results in floating segregation of the largest atom during growth. The strength of floating segregation is determined by an interplay between surface-energy difference, size difference, and mixing energy. Essentially, floating segregation is shown to be an effect that is limited to the surface, which occurs in addition to the Ex-1 and Ex-2 mechanisms during growth, and it does not affect the final interface profile of the layered structure. As a special case, Cu exhibits floating segregation behavior in both TM-on-Cu and Cu-on-TM systems, as long as the TM is not a large atom like Sc.

3. There is a unique exponential trend in the interface width as a function of the surface-energy difference for each crystal structure combination, which serves as a scaling law to predict the intermixing in TM-on-TM systems. In general, bcc TMs intermix less when compared to hcp and fcc TMs because of higher bond strength of bcc atoms.

As an overall conclusion, the proposed general rule for predicting the growth profile type and the proposed scaling law for predicting the effective interface width, together provide the possibility to predict the growth and interface characteristics in TM-on-TM systems. This opens a new field of possibilities in controlling the quality of interfaces in thin-film structures, and it is expected to have a direct impact on the development of applications where the interfaces are critical for the device performance.

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