### **Supporting Information**

## Identifying silicides via plasmon loss satellites in photoemission of the Ru-Si system

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#### S1: GI-XRD 2D diffraction pattern of (Ru₂Si₃+RuSi)-PLD

In figure S1 the GI-XRD 2D detector image is shown of the sample ( $Ru_2Si_3+RuSi$ )-PLD. The blue outline is the detector integration area. The white arrow indicates the saturated pixels underlying the peak marked by an asterisk (\*) at a diffraction angle (20) of 40° in Figure 1. The blue arrow shows the diffraction ring corresponding to the peak at a diffraction angle (20) of 55°.

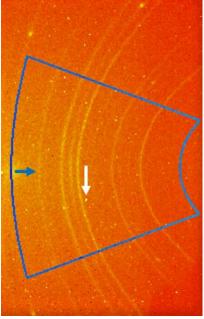


Figure S1: 2D diffraction pattern of ( $Ru_2Si_3+RuSi$ )-PLD. Raw data of the diffractogram reported in Figure 1.

# S2: XPS Si 2p peak fitting parameters

Table S1 Peak fitting parameters of the Si 2p species: Si,  $Ru_2Si_3$ , and RuSi, using Voigt doublets with the following parameters: binding energy position (Pos), Lorentzian line width (Lwid), Gaussian line width (Gwid), spin-orbit split (Split).

| -          | Si (Si 2p) | Ru₂Si₃ (Si 2p) | RuSi (Si 2p) |
|------------|------------|----------------|--------------|
| Pos (eV)   | 99.4       | 99.7           | 100.0        |
| Lwid (eV)  | 0.07       | 0.18           | 0.25         |
| Gwid (eV)  | 0.71       | 0.46           | 0.45         |
| Split (eV) | 0.63       | 0.62           | 0.62         |

## S3: Depth-dependent atomic ratio determination using Ru 3p, Ru 3d, and Ru 4p

The peak areas of the Ru 3p, Ru 3d, Ru 4p, and Si 2p core levels have been determined from XPS survey spectra for all samples. The kinetic energies of the Ru  $3p_{3/2}$ , Ru  $3d_{5/2}$ , and Ru  $4p_{3/2}$  photoelectrons are 1024 eV, 1206 eV, and 1443 eV, respectively, resulting in the highest probing depth for Ru 4p, followed by Ru 3d and Ru 3p. Table S2 shows the measured Ru content corrected for photoemission cross section and probing depth. The values are normalized to the result for Ru 3d. The lower Ru signal for Ru 4p and higher Ru signal for Ru 3p is particularly pronounced for the samples containing the RuSi phase, indicating Ru enrichment in the surface region for these samples.

Table S2 Ru intensities determined by XPS of Ru 4p, Ru 3d, and Ru 3p for the samples Ru-Si(100), RuSi-PLD, (Ru<sub>2</sub>Si<sub>3</sub>+RuSi)-PLD, (Ru<sub>2</sub>Si<sub>3</sub>+Si)-PLD and Ru<sub>2</sub>Si<sub>3</sub>-Si(100).

|   | Ru 4p | Ru 3d | Ru 3p |
|---|-------|-------|-------|
| Ru <sub>2</sub> Si <sub>3</sub> -Si(100)  | 0.85  | 1.00  | 1.04  |
| (Ru₂Si₃+RuSi)-PLD                         | 0.80  | 1.00  | 1.18  |
| RuSi-PLD                                  | 0.80  | 1.00  | 1.26  |
| (Ru <sub>2</sub> Si <sub>3</sub> +Si)-PLD | 0.71  | 1.00  | 0.99  |
|   |       |       |       |