Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information.

Sample Preparation:

Silica thin films containing homogeneously dispersed Co atoms deposited on Si(001), Si(111) and Si(011) wafers were obtained by dipping the flat surface of the Si substrates into a solution of cobalt(II) nitrate (11 μmol/g) and tetraethylorthosilicate (TEOS, 240 μmol/g) in isopropanol. After evaporation of the solvent the films were dried during 10 min at 100 C and calcined during 15 min at 500 C. In order to promote the chemical reduction of the precursor molecules thus inducing the formation of Co atoms, the samples (thin film and substrate) were isothermally treated during 1 hour at 500 C under H_2 atmosphere to promote the Co oxide reduction. Finally all samples were subjected to an equivalent isothermal annealing during 1 h at 750 C under He atmosphere. This last thermal process allowed for the diffusion Co atoms thus promoting: (i) the aggregation of Co atoms and further formation of Co nanoparticles (NP) embedded in the SiO_2 thin film and (ii) the formation of $CoSi_2$ nanoplatelets buried in the Si wafer.

TEM figures:

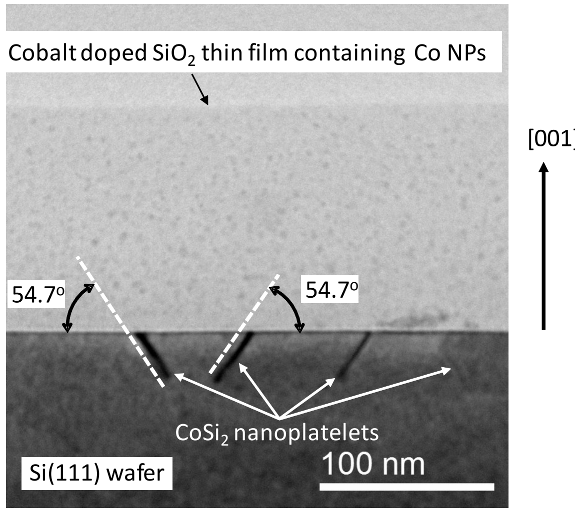

Figure 1: TEM image corresponding to a SiO_2 thin film deposited on a Si(001) wafer. A number of small Co nanoparticles embedded in the thin SiO_2 and three $CoSi_2$ buried in the Si wafer are apparent. The rotation ϕ angle was selected trying to maximize the contrast of the nanoplatelets with respect to the host matrix; this occurs when the electron beam is parallel to main face of the nanoplatelets. The angle between the nanoplatelet faces and the external wafer face is 54.7º, which corresponds to the angles between the (001) plane and those of the {111} form.

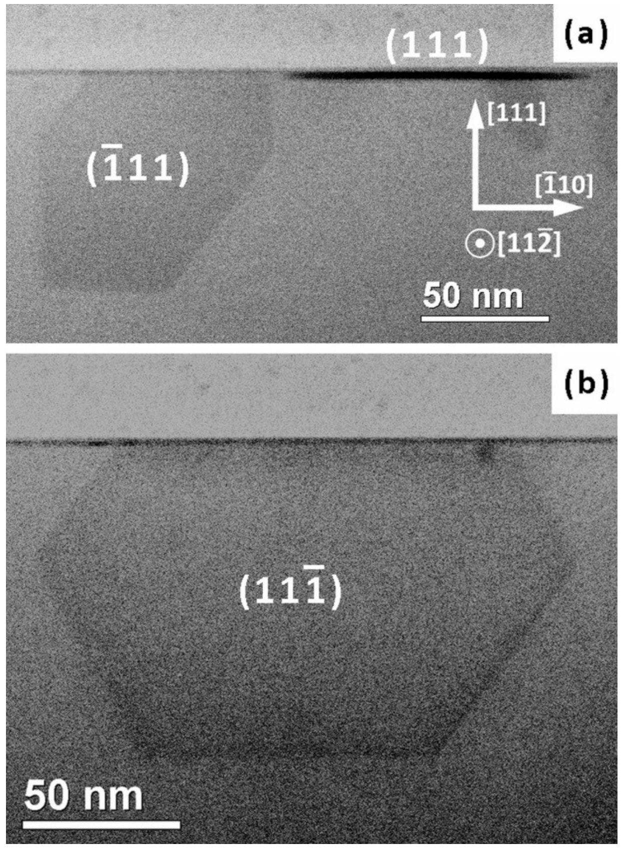

Figure 2: STEM bright field images corresponding to SiO_2 thin film with Co nanoparticles deposited on Si(111) wafer, observed along the [11-2] zone axis. A nanoplatelet lies on the surface of the wafer, i. e. $\alpha = 0$, at the (111) plane. One can observe a nanoplatelet in a front-view at the (11-1) plane and another one at the (-111) plane.

Stereographic projections

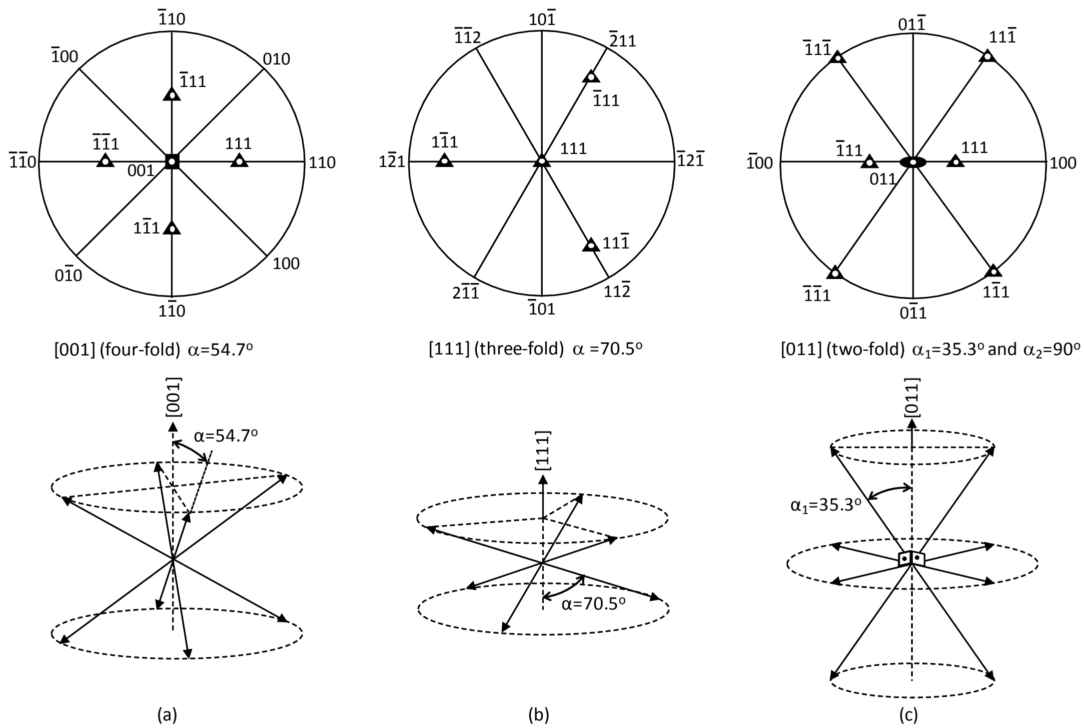

Figure 3: above: picture showing the stereographic projections of crystallographic planes of the cubic Si{111} form, corresponding to wafers (a) Si(001), (b) Si(111) and (c) Si(011). Below: Spatial views of {111} directions for the three studied Si wafers.

Schematic GISAXS setup:

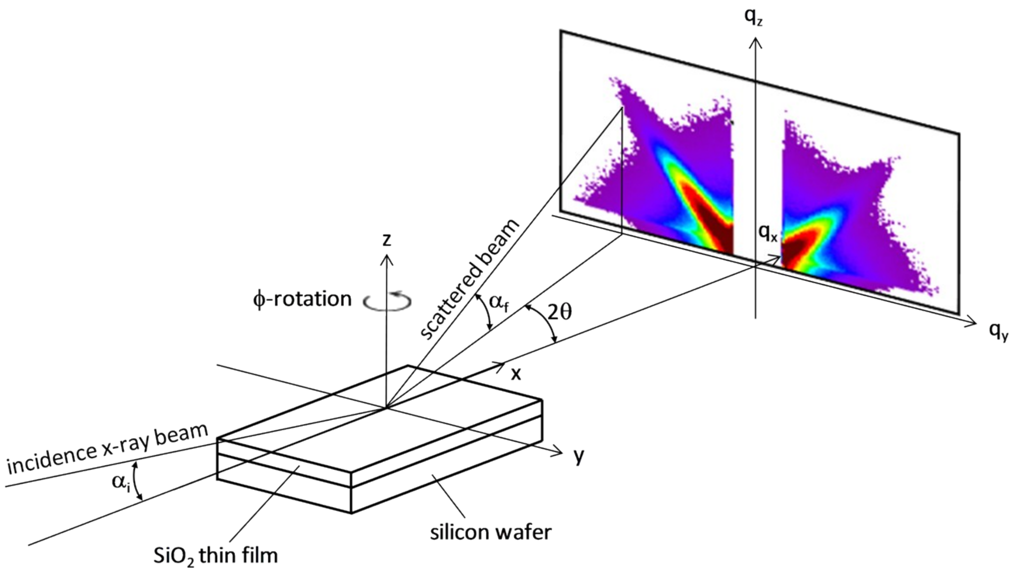

Figure 4: schematic GISAXS setup. The relevant angles and directions are indicated.

In the geometry represented in figure 3 the scattering or transferred moment vector $\vec{q}$ is given as

$$\vec{q} = \vec{k}_f - \vec{k}_i = \frac{2\pi}{\lambda}\begin{pmatrix} \cos 2\theta_f \cos \alpha_f - \cos \alpha_i \\ \text{sen } 2\theta_f \quad \cos \alpha_f \\ \text{sen } \alpha_f + \text{sen } \alpha_i \end{pmatrix} \tag{1}$$

where $\vec{k}_i$ e $\vec{k}_f$ are the wavevectors of the incoming and scattered X-ray beams, respectively, λ is the X-ray wavelength, α_i and α_f are the angles of the incident and scattered beam, respectively, with respect to the external sample surface, and $2\theta_f$ is the angle between the projection of the scattering vector on the sample surface and the *x*-direction (see figure 3).

The general theory of X-ray scattering indicates that the scattering intensity in reciprocal space, associated to a thin nanoplatelet, is concentrated within a narrow lobe with its major axis normal to the nanoplatelet main faces. Assuming that both sets of nano-objects (nanoparticles and nanoplatelets) scatter independently, the total GISAXS intensity is given by

$$I \propto \left|t(\alpha_i)\right|^2 \left|t(\alpha_f)\right|^2 \left(c_R \int \sum_{kkl} \left| A_{hex(hkl)}(\alpha, \phi, q_x, q_y, \widetilde{q}_z, \mathsf{l}, t) \right|^2 N_t(t) dt + \int \left| A_{sph}(q_x, q_y, \widetilde{q}_z, R) \right|^2 N_{sph}(R) dR \right), \qquad (2)$$

where $t(\alpha_i)$ and $t(\alpha_f)$ are the Fresnel transmission coefficients for the incoming and scattered beams, respectively, c_R is a factor proportional to the number of hexagonal nanoplatelets, $N_{sph}(R)$ is the function defining the radius distribution of Co NP, $N_t(t)$ is the normalized function describing the thickness distribution of $CoSi_2$ plates, $A_{sph}(q_x, q_y, \widetilde{q}_z, R)$ is the scattering amplitude of a spherical NP with radius R given by

$$A_{sph} = 4\pi R^3 (\rho_p - \rho_m)[\sin(qR) - qR\cos(qR)]/(qR)^3 \qquad (3)$$

and $A_{hex(hkl)}(\alpha, \phi, q_x, q_y, \widetilde{q}_z, \mathsf{l}, t)$ is the scattering amplitude of an hexagonal nanoplatelet with lateral side l and thickness t. The *hkl* indexes in the sum of the Eq. (2) are labels for the different orientations of the nanoplatelets defined by the directions normal to the Si{111} crystallographic planes. In the same equation, α is the angle between the incoming X-ray beam and the external surface of the Si wafer and ϕ the azimuthal angle.