

# Inhibiting the segregation of germanium in silver nanolayers

## Supporting information

The atomic concentrations of sample components were estimated by using CasaXPS® software (version 2.3.16). The most intensive peaks for each element of the sample were recorded. In case of metals it was Ag3d and Au4f levels. In the case of germanium, only part of Ge2p doublet - Ge2p<sub>3/2</sub> was used for calculation due to a high spin-orbit split (in that case over 31 eV). In order to obtain the intensity of these peaks the experimental data was fitted to Gauss-Lorentz shapes and to get the information about concentrations of the components the relative sensitivity factors (RSF) for each element from CasaXPS library were used. According to the authors' knowledge, the CasaXPS RSF library is based mostly on Scofield cross-sections calculated from Hartree-Slater approximations. The software version available to the authors does not offer any escape depth correction during quantification. Different values of escape depth might influence the absolute values of atomic concentration of elements, but it does so with the same multiplicative factor for every sample and for all etching times, thus the tendencies discussed in the paper are viable and different samples can be compared.

For example, for the SiO<sub>2</sub>/20 nm Au/2 nm Ge/20 nm Ag/3 nm LiF sample measured 30 days after deposition, the total area under Ge2p<sub>3/2</sub>, Ag3d<sub>5/2</sub> and Au4f<sub>7/2</sub> are respectively: 117165.6, 277870.8 and 1999.2. Their RSF-s are respectively: 24.2, 10.7 and 9.58 (with respect to C1s RSF = 1). In order to estimate Ge to metal ratio, peak areas are divided by adequate RSF resulting with 4841.6 (Ge), 25969.2 (Ag) and 208.7 (Au). In this example, Ge to Ag ratio is therefore about 0.19 and Ge/Au 23.2. In order to estimate atomic concentrations one has also to include other components, such as oxygen, fluoride and carbon (lithium intensity was below detection level) and use the formula:

$$c_i = \frac{I_i/R_i}{\sum_i (I_i/R_i)} \cdot 100\%$$

where  $c_i$  is the concentration of  $i$ -th component,  $I_i$  - area of its peak and  $R_i$  - its RSF. In case of this example concentrations of Ge, Ag and Au were respectively 4.2%, 22.3% and 0.2%.

There was no clear correlation between chemical shifts of Ag or Au lines and concentration of germanium. Binding energies of Au4f and Ag3d levels vary slightly ( $\pm 0.2$  eV) and these variations are rather a result of imperfect charge compensation than true chemical shift caused by Ge presence, thus these shifts were not considered during data curation.