

# Producing Cu-Ag core-shell nanoparticles by spinodal decomposition

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Nanocomposites can have wide variety of morphologies from designed multilayers to self organized layered structures through columnar and globular morphologies including core-shell and alloy nanoparticles of different stable and metastable phases of the components. The demand to understand morphological development in these nanostructures gained an increasingly growing importance as the two- and multicomponent films have achieved their application in many fields like hard and wear resistant coatings. Both alloy and core-shell structures are of great interest for their chemical, optical and optoelectronic properties. Preparation of bimetal alloy films and nanoparticles by co-deposition and their formation mechanisms are studied in this work including phase separation by spinodal decomposition, transforming the alloy particles to core-shell composite ones.

In order to be able to examine phase separation, we were aiming for a model system where simultaneous deposition causes metastable structures. This is the reason for choosing the Cu-Ag system, which has a wide miscibility gap.

Cu-Ag films were created in several compositions (30-80 at.% Ag) by magnetron sputtering on a thin carbon substrate or oxidised (100)Si wafers, in  $8 \cdot 10^{-8}$  mbar background vacuum. The effective thickness of the films was 1-500 nm. The composition was varied by calibrating the sputtering rate of Cu and Ag targets as the function of sputtering power. With the help of high resolution electron microscopy, we examined the morphology, surface and internal structure of the materials. Kinetic Monte Carlo simulations were carried out to model atomic diffusion in alloy particles of 2-8 nm in size.

Spinodal decomposition in thicker Cu-Ag films has been found a working atomic mechanism of the nanocomposite structure formation at compositions close to eutectic (65 at% of Ag) [1]. For the thinner films in the coalescence stage liquid like coalescence resulted in random polycrystalline islands due to crystallization from melt [1]. In the present work phase separation in island films preceding coalescence has also been investigated.

One-phase particles (single crystals or multiply-twinned crystals) could be identified in films of higher Ag content (above 50 at%). The presence of these particles in the films shows, that decomposition in these sizes is not occurring in all conditions and compositions (or is hardly detectable). In films of lower Ag content nearly half of particles have decomposed, and both domains containing Cu and Ag in majority were identified by measuring the lattice parameters in the high resolution images. We suggest that the decomposition took place by spinodal decomposition. The high-resolution electron microscopy images clearly demonstrate that Ag tends to accumulate in the near surface regions, while Cu majority domains remain in the core of the particles.

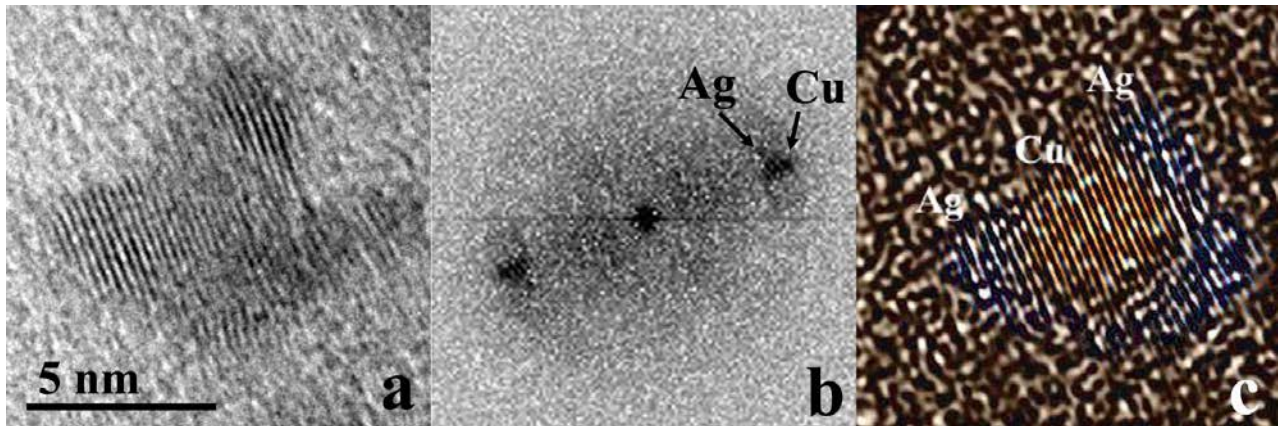
Kinetic Monte Carlo simulations were also used to model the separation processes observed. Our results show that phase separation processes begin even in the 2-3 nm size range and can provide core-shell type nanoparticles. Simulations also supported the observation that Ag accumulates in the near surface area due to surface segregation, and that decomposition takes place by spinodal way.

Finally we can conclude, that alloy and two phase nanoparticles can be produced by co-deposition of components having broad miscibility gap in the phase diagram. In the case of Cu-Ag alloy nanoparticles, preferably at composition of 30 at% of Ag, two phase particles can form, resulting in core-shell like morphology. Kinetic Monte Carlo simulations support the high resolution microscopy observations and predict phase separation even at compositions of higher Ag content, close to the eutectic [2].

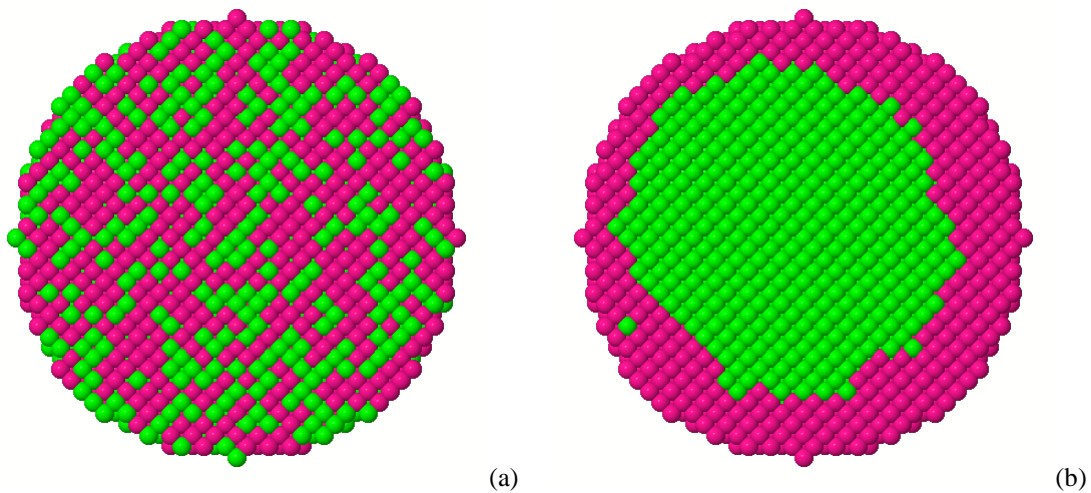
## References

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**Figure 1.** A few nm in diameter Cu-Ag (30 at % of Ag) particle, showing phase separation. Overall view of the particle (a), Fourier transform of the image in (a) showing practically complete separation as measured from lattice parameters (b) and the location of Ag (blue) and Cu (orange) domains in a core shell particle obtained by spinodal decomposition (c).



**Figure 2.** Snapshots of phase separation in two-component (60% Ag) hemispherical nanoparticle with a diameter of 8 nm obtained by Kinetic Monte Carlo calculations: cross section of initial state, random alloy (a); after complete separation (b).