Report on the experiment 08-01-195:
Metal alloy nanocluster formation in double implanted silica glass: an EXAFS study.

The aim of the proposed experiments was to determine the local order around the metal species forming nanoaggregates within silica matrix upon ion implantation, so investigating the role of different preparation parameters in giving rise to different cluster structures.
This was accomplished by EXAFS analyses on Au+Ag, Au+Cu, implanted silica slides.
The following points were established.

Au+Ag implanted silica.
Gold implantation in silica (3*10^16 ions/cm^2, ion energy=190keV) determines the formation of gold nanoclusters; in the examined case, a shrink of the nearest-neighbor distance is observed with respect to gold crystal, probably due to the reduced cluster size, about 2-3 nm. Moreover, part of implanted atoms remained dispersed in the matrix.
Subsequent silver implantation (ion energy=130KeV) leads to the aggregation of gold-silver alloy nanocrystals; silver ions feed gold clusters and the alloy is the dominant phase in the system (possible oxide phases or single-metal clusters, if present, are marginal). The alloy composition depends on Ag implantation fluence: in particular, it respects the nominal implanted concentration only for high Ag fluence, while for equal Au and Ag implantation fluence the alloy results rich in gold, probably because part of silver atoms remain dispersed in the matrix.
Upon thermal annealing at 800°C for 1 hour, significant changes in the dopant concentration are not detected. Nevertheless, the alloy composition is shifted toward 1:1 ratio, thus respecting the relative implantation fluences; this occurs independently of the atmosphere used in the annealing process (reducing or oxidizing): in fact, almost the same mean alloy composition is found after 1 hour annealing. This clarifies the fact that upon thermal treatment the final structure of the composite is not driven by the presence of oxygen atoms from the atmosphere but by the silver diffusivity into the Au-rich alloy clusters: this is due to the low gold and silver reactivity toward oxygen atoms. Also in this case, other phases different from the alloy, if present, are marginal.

Au+Cu implanted silica.
Au-Cu alloy nanoclusters (whose corresponding bulk phase is thermodynamically stable in the whole composition range) are formed after copper implantation on silica (dose=3-6*10^16 ions/cm2, ion energy=90keV) containing gold nanoclusters (formed by Au implantation). A possible mechanism for the alloy formation is the radiation-enhanced diffusion of copper into small gold clusters during copper implantation: this determines both the alloy formation and the cluster growth. The alloy composition depends on the implantation fluence (for fixed implantation energy) as well as on the copper reactivity toward oxygen atoms. In Au+Cu-implanted silica with equal doses, the alloy is rich in gold, since part of implanted copper atoms is dispersed in the matrix. The increase of the Cu implantation fluence makes the cluster composition to shifts toward Cu-rich alloy: the reason is both the higher copper concentration in the matrix and possibly the enhancement of its diffusivity by the implantation process.
The analyses on two Au+Cu implanted samples after annealing in reducing atmosphere at 900°C suggest that the nanocrystal alloy phase, that in both cases was fcc with different alloy composition before annealing, moves toward a super-ordered tetragonal phase (evidenced by Cu-Au-Cu correlation on Cu K-edge EXAFS spectrum) where the local concentration of the two metal is balanced. That is, in the sample implanted with equal Au and Cu ions doses, the annealing makes the dispersed Cu atoms to move into the Au-rich alloy clusters, so balancing their composition: the tetragonal phase is in this case the major crystalline structure. For the sample in which the copper fluence is doubled with respect to gold, after annealing the tetragonal structure is present as a minor phase, probably in the sample zone where the redistributed local concentration of the two metals is balanced; the most important phase is in this case formed by a Cu-rich solid solution alloy clusters.

It is still not clear if the transition from an fcc solid solution to a super-ordered structure (tetragonal) occurs by melting of the clusters. In fact, a decrease of the melting temperature with respect to the bulk phase could occur, due to the surface energy contribution to the Gibbs energy of the system.
In the system containing mostly Cu-rich solid solution alloy, EXAFS results suggest a deviation of the crystal structure from the virtual crystal approximation: that is, the crystal
structure is fcc, but the atoms are slightly displaced from their positions. This behavior was already evidenced and theoretically expected in bulk fcc solid solution alloys (AuxCu(1-x), AuxNi(1-x)), in which there is a remarkable lattice mismatch between the crystals of the two alloy components; further analysis should be made on this subject, to better quantify the phenomenon,
to our knowledge never observed before, and to test the theoretical models proposed for the bulk.
The alloy nanoclusters are not stable under annealing in oxidizing atmosphere (air): 1h treatment at 900°C results in the alloy segregation. This behavior, completely different from that of Au+Ag implanted sample processed in similar conditions, depends on the high reactivity of copper with the oxygen atoms from the annealing atmosphere; actually, oxygen atoms drive copper out of the alloy clusters and toward the surface; part of copper leaves the sample and the rest is oxidized near the surface mainly as crystalline CuO. Still part of Au and Cu did not aggregate in clusters.