ESRF	**Experiment title:** Metal-induced crystallization of a wurtzite Silicon phase in *a*-Si film: an EXAFS study on the role of Chromium .	**Experiment number**: **SI-2050**
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Preliminar Report

Aim of the experiment

Aim of the present project was to study the local coordination of Cr during the various phases of low-temperature metal-induced crystallization (MIC) of *a*-Si films in differently prepared samples. The research is a continuation and a development of our previous studies on Ni-doped *a*-Si films, where EXAFS was able to document that diluted Ni atoms immediately tend to coordinate as in $NiSi_2$, producing dispersed nucleation centers for c-Si. Recently, we focused the attention to a-Si films with Cr diffusing from the top, where instead of the usual cubic c-Si phase, RAMAN spectroscopy and TEM showed evidence of an hexagonal wurtzite phase.

The present EXAFS studies aimed at determining the local order and the coordination of Cr before and after the crystallization onset of different *a*-Si films. The aim of the EXAFS study is to determine the local environment (co-ordination type, first shell distance, order, strain) around the Metal impurity and to correlate it to the appearance of different phases of c-Si in the film. These structural data will be combined with the results of Raman spectroscopy to study the amorphous/crystal phase transition. We expected to document the appearing and diffusion of crystalline seeds around Cr atoms, always keeping in mind the likely appearance of precursor silicides. We aimed to compare samples prepared in very different configuration: thus we expected to document the differences and to describe the fundamental of MIC, together with the parameters that influence the presence of different c-Si phases.

Experimental

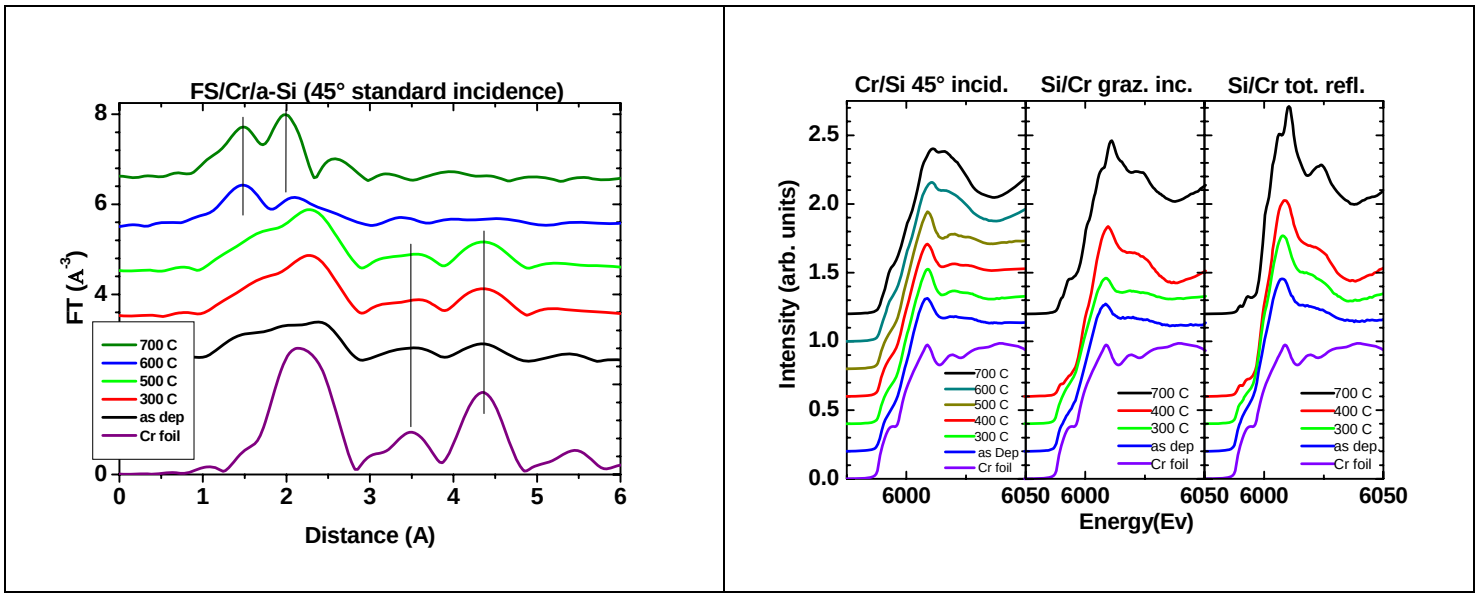
Chromium and Silicon films were deposited by electron beam evaporation on to fused silica (FS) substrates in high vacuum of the order of 10^{-6} Torr. The starting materials were granular pure silicon powder (99.999%) and Cr powder (99.99% pure). First a 50 nm thin Cr blanket bottom layer was deposited on FS substrates maintained at ambient temperature. This is followed by the deposition of a 400 nm thick Si film, without breaking vacuum, to form a FS/Cr/Si stack. Later on, the films were annealed in a N_2 rich atmosphere at different temperatures for 1 hr. Similarly, different FS/Si/Cr stacks were prepared with substrate at ambient as well as at higher temperatures.

EXAFS fluorescence measurements were carried out at Cr K edge in these different geometries, depending of course on the samples: a) for the FS/Cr/Si stacks, at standard 45° incidence geometry; b) in total reflection (TR) geometry; c) just behind the critical angle;

Main results

A quantitative analysis will be done in the future. At present, we may describe qualitatively the main changes in XANES and EXAFS spectra.

A first interesting information is on the as deposited Cr layers, in both Cr/Si and Si/Cr configuration. The EXAFS signal is quite low in comparison with Cr foil, indicating a high degree of static disorder. However, both samples show in the FT evidence of the first three coordination shells as in met-Cr, with very similar imaginary part, except for the shorter distances where Cr-Si or Cr-O bonds should be present.



It is interesting to note that EXAFS in standard incidence on samples with Cr deposited below a-Si show a progressive ordering of coordination shells with respect to the as deposited sample, without significant structural changes up to 500 C of thermal treatment (30' in nitrogen atmosphere). At 600 C the situation is totally changed, with the disappearance of the contribution of longer Cr-Cr distances and the growing of Cr-Si and Cr-O bonds within a complex "first shell peak". After 700 C, the Cr-Si contribution at about 2.0 Å is predominant, however with significant intensity of peaks centered at 1.5 and 2.6 Å, that at present we attribute to Cr-O bonds. The thermal behavior is confirmed by the analysis of XANES, that are strongly modified only in samples treated at 600 and 700 C.

Samples with Cr diffusing from bottom were tested on total reflexion, but only the sample heated at 500 C for a very long time (15 h) showed a little, but detectable fluorescence signal from Cr, whose complex XANES and EXAFS spectra are under analysis.

The XANES analysis is quite useful also to qualitatively describe the Cr environment in the Cr layer deposited on top as a function of thermal treatment. We have investigated these layers at two slightly different incidence angles, thus we can monitor either just the few nanometers on top in total reflection or a thicker layer. It is clear that in TR XANES are more sensitive to possible surface oxidation, clearly detectable also in the as deposited samples, but only as contaminant. However, analysis of the pre-edge structures shows that Cr_2O_3 environment is prevailing only in the sample treated at 700 C and measured in TR. In the inner layer and in all the other samples, XANES documents that the diffusion of met-Cr particles starts only at T higher than 400 C, while at present it is not clear when Chromium Silicides appear and grow.

Quantitative EXAFS analysis is in progress to disentangle the following three main processes: a) at first thermal ordering of metallic layer and then Cr diffusion; b) reaction of Cr with Si to form silicides; c) oxidation process, that seems to appear also in vacuum annealed samples (i.e. it is a post-annealing process).

Conclusions and future work

In both Cr/Si and Si/Cr films deposited at higher temperature and also in post annealed samples Chromium diffuses and forms silicides with some part oxidized. The chemistry of Cr is found to change suddenly beyond 500 °C annealed samples. Quantitative analysis is in progress. Complementary characterizations by SIMS and XPS are also scheduled on all the measured samples. A parallel study on Ni-doped a-Si is currently going on: a new proposal has been already submitted at ESRF (Sept. 2010).