Metal induced crystallization of amorphous silicon thin films studied by x-ray absorption fine structure spectroscopy

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Abstract. The role of thin metallic layer (Chromium or Nickel) in the crystallization of a-Si film has been studied using X-ray absorption fine structure spectroscopy (XAFS). The films were grown at different substrate temperatures in two different geometrical structures: (a) a 200 nm metal layer (Cr or Ni) was deposited on fused silica (FS) followed by 400 nm of a-Si and (b) the 400 nm a-Si layer was deposited on FS followed by 200 nm of metal layer. XAFS measurements at Cr K-edge and Ni K-edge were done at BM08 - GILDA beamline of the European Synchrotron Research Facility (ESRF, Grenoble, F) in fluorescence mode. To understand the evolution of the local structure of Cr/Ni diffusing from bottom to top and from top to bottom, total reflection and higher incidence angles were employed. The relative content of metal, metal oxide and metal silicides compounds on the upper surface and/or in the bulk of different films has been evaluated as a function of thermal treatment.

1. Introduction
Amorphous silicon crystallizes at 750 °C, or higher, temperature [1]. The crystallization temperature can be strongly reduced (in the range 165-300 °C) by low-doping with metals or by depositing a thin metal layer onto a-Si film [2]. The mechanism is known as Metal Induced Crystallization (MIC). Various conflicting explanations for the MIC phenomenon have been discussed in the literature [3]. Aim of the present work is to investigate the evolution of the local environment of two metal dopants (Cr or Ni) deposited at different substrate temperatures below or above a layer of a-Si using X-ray absorption fine structure (XAFS) technique. The result is a detailed study of changes with temperature around Cr or Ni, due to different metal diffusion and to the formation of new silicide phases.

2. Experimental and data analysis methods.
Films composed of two nominal layers were deposited onto fused silica (FS) substrates using electron beam evaporation at 4 x10⁻⁶ torr in both possible combinations: Cr or Ni (nominal 200 nm) metals were deposited before (i.e. on bottom) or after (i.e. on top) the deposition of a 400 nm thick a-Si layer. The starting materials were granular pure Silicon powders (99.999%), Chromium granules (99.99% pure) and Nickel granules (99.99% pure). The films were annealed for 30 min inside the vacuum chamber at the different substrate temperatures selected for the deposition. The deposition conditions were decided in order to discriminate: a) the possible different diffusion rate from bottom up to the surface of metals; b) the influence of temperature on chemical reactions of metals with a-Si. In parallel studies, we already showed that the Cr films deposited at 200 °C do not contain significant modifications in the metal chemistry, because changes appear only at higher deposition or annealing.
temperature [4]. We present here results on films deposited at 200 °C or 500 °C below a-Si, while 400 °C has been selected for deposition above a-Si, to reduce oxidation effects.

XAFS measurements of the films were performed at Cr or Ni K-edges (5989 eV and 8400 eV respectively) in fluorescence mode with a Ge multidetector at BM08-GILDA (ESRF, France) [5]. Total Reflection geometry was used, when possible, to study the metal environment near the surface, while different higher incidence angles were selected to investigate the whole sample [6]. Reference samples for Cr edge were measured in transmission mode at the XAFS beamline of ELETTRA (Trieste, Italy). Later the energy axis of the spectra was carefully aligned with respect to the energy axis of XAS spectra of a Cr foil measured at GILDA. Reference materials for Nickel where measured in transmission mode at GILDA.

Quantitative analysis of EXAFS has been carried out using FEFF8 and FEFFIT codes [7,8]. Details of theoretical calculations are deeply discussed and commented in parallel papers [4,9]. In summary, the FT-EXAFS spectra of films were best-fitted using a set of fixed distances (R) and coordination numbers (N) as pre-determined by studying the crystal structure of reference materials; thus the best fit was a simple linear combination of the minimal number of shells of the reference materials, each of them having a free DW factor. The fit results give us the relative content of metal, oxide and silicides present in the investigated sample region.

3. Results

3.1 EXAFS analysis of Reference materials

The reference compounds were metallic foils of Cr and Ni, and Cr2O3, CrSi2, NiO, Ni2Si, NiSi2 powders, measured in transmission in optimal standard conditions. The E0 and S02 values of each reference compound were carefully evaluated through FEFFFIT analysis and used later as fixed parameters for the best fit of films, whose EXAFS was extracted using E0 of metals. In particular, we determined E0 as 5992 eV for metallic Cr, 5998 eV for Cr2O3, 5996 eV for CrSi2, 8337.5 eV for metallic Ni foil, 8342 eV for NiO, 8341 eV for Ni2Si and 8337.8 eV for NiSi2.

We considered the following shells to fit the spectra of the references at the corresponding distances R (and coordination numbers N): to fit metallic Cr six Cr-Cr shells; to fit Cr2O3 three Cr-O shells and four Cr-Cr shells; to fit CrSi2 three Cr-Si shells and two Cr-Cr shells.

Similarly, to fit metal Ni spectra we considered seven Ni-Ni shells; to fit Ni2Si three Ni-Si shells and six Ni-Ni shells; to fit NiSi2 one Ni-Ni shell and five Ni-Si paths; for NiO we considered three Ni-O shells, three Ni-Ni shells and five multiple scattering (MS) paths.

The obtained S02 values were used to evaluate later the relative content of these reference compounds in the investigated films.

3.2 EXAFS analysis of films with Cr

Figure 1 shows near edge x-ray absorption spectra (NEXAFS) of films deposited at 200 °C and 500 °C with Cr as bottom layer and deposited at 400 °C with Cr as top layer along with the reference samples. The EXAFS Fourier transforms (FT) with the best fits in dotted line are shown in Figure 2. The film deposited at 200 °C has only partial resemblance with metallic Cr spectrum, suggesting the presence of other Cr compounds along with metallic Cr. On the film deposited below a-Si at 500 °C, we did not detect any fluorescence signal when probed in TR geometry, indicating that Cr was not able to diffuse up to the surface of the film. The two EXAFS spectra of film deposited at 500 °C probed at 10° and 45° have similar features. Both the spectra can be reproduced by a linear combination of shells from CrO3 and CrSi2. The relative percentage of Cr compounds obtained from the EXAFS quantitative analysis are presented in Table 1, with error bars estimated on the basis of different extractions and best fit procedures. From Table 1 we may note that, for the film deposited above a-Si at 200 °C, only a small fraction of Cr metal reacted with a-Si during deposition to form CrSi2, but we have quantified a significant fraction of Cr in oxidized state. When the substrate temperature is raised to 500 °C, the
bottom metal layer contribution disappears and a larger fraction of Cr is transformed into CrSi₂ and Cr₂O₃. Since Oxygen was totally absent in the deposition chamber, we explain the Cr₂O₃ formation as due to a successive oxidation of metal atoms or nanoparticles diffused inside the a-Si layer, but unreacted and highly unstable. The TR spectrum of film deposited on top at 400 °C shows on the surface the typical features of both Cr₂O₃ and metallic Cr, while the corresponding one at 10° shows a complete absence of Cr₂O₃, (note the absence of the peak of Cr-O at 2 Å in the FT), and the presence of the features of metallic Cr and CrSi₂. From Table 1 it may be observed that on the surface about 50% of unreacted Cr was oxidized, while a large part of Cr atoms diffused into the a–Si layer were stabilized in met-Cr nanoclusters, or able to react forming a more stable CrSi₂ compound.

![Figure 1 Cr K edge XANES of FS/Cr (200 nm)/a-Si (400 nm) stack deposited at 200 °C and 500 °C, and of FS/Si (400 nm)/Cr (200nm)stack deposited at 400 °C, along with those of metal Cr, Cr₂O₃ and CrSi₂.](image1)

![Figure 2 FT EXAFS signal of FS/ Cr (200 nm)/ a-Si (400 nm) stacks at 200 °C and 500 °C, and of FS/Cr (200 nm)/ a-Si (400 nm) stack at 400 °C, along with those of the three references. The best fits of FT signals are shown by dotted lines.](image2)

### Table 1

The percentage of different Cr compounds present in films with Cr as bottom and top layer in a-Si films.

| Sample               | Cr (%)   | Cr₂O₃ (%) | CrSi₂ (%) |
|----------------------|----------|-----------|-----------|
| FS/Cr/a-Si 200°C 45° | 64 ± 10  | 21 ± 10   | 15 ± 10   |
| FS/Cr/a-Si 500°C 10° | ---      | 48 ± 10   | 52 ± 10   |
| FS/Cr/a-Si 500°C 45° | ---      | 62 ± 10   | 37 ± 10   |
| FS/a-Si/Cr 400°C TR  | 55 ± 10  | 45 ± 10   | ---       |
| FS/a-Si/Cr 400°C 10° | 61 ± 10  | ---       | 39 ± 10   |

### 3.3 EXAFS analysis of film with Ni

The XAS and FT of films with Ni as bottom layer deposited at 200 °C and 500 °C, and with Ni as top layer deposited at 400 °C are shown in figure 3 and figure 4. The films were probed at 2° and TR mode. The quantitative results are shown in Table 2. The film deposited at 200 °C appears to contain almost metal Ni. Contrary to the Cr case, on the surface investigated by TR spectrum, we could detect Ni atoms diffused from the bottom layer, in met-Ni clusters or partially reacted with a-Si to form Ni₂Si. The film deposited at 500 °C contains combined features of NiSi₂ and NiO in the whole layer. As substrate temperature is raised to 500 °C, metal Ni not only diffuses into a-Si layer towards the upper surface of the film, but there is an increasing formation of NiSi₂. From the TR spectrum it is shown that about 75% of metal Ni at the surface of the film evolves as NiSi₂. The remaining 25% Ni is embedded in the NiSi₂ layers.
The films with Ni top layer at 400 °C had resemblance with NiO and metal Ni. It is clear from the analysis that Ni is unable to react with Si to form NiSi2. The amount of Ni oxidation is more on the surface, with NiO about 77% on surface and about 56% inside the film.

![Figure 3](image1.png)  
**Figure 3** Ni K edge XAS of FS/Ni (50 nm)/a-Si (400 nm) stacks deposited at 200 °C and 500 °C, and FS/Si (400 nm)/Ni (50 nm) stack deposited at 400 °C, along with those of metal Cr, Cr2O3 and CrSi2.

![Figure 4](image2.png)  
**Figure 4** FT EXAFS signal of FS/ Ni (50 nm)/a-Si (400 nm) stacks deposited at 200 °C and 500 °C, and of FS/Ni (50 nm)/a-Si (400 nm) stack deposited at 400 °C, along with those of three references. The best fits of FT signals are shown by dotted lines.

### Table 2

| Sample       | Ni (%) | NiO (%) | NiSi2 | NiSi |
|--------------|--------|---------|-------|------|
| FS/Ni/a-Si   | 200°C TR | 57 ± 10 | ----  | 43 ± 10 |
| FS/Ni/a-Si   | 200°C 2° | 100     | ----  | ----  |
| FS/Ni/a-Si   | 500°C TR | 25 ± 10 | ----  | 75 ± 10 |
| FS/Ni/a-Si   | 500°C 2° | 51 ± 5  | ----  | 49 ± 5  |
| FS/a-Si/Ni   | 400°C TR | 23 ± 10 | 77 ± 10 | ---- |
| FS/a-Si/Ni   | 400°C 2° | 44 ± 5  | 56 ± 5  | ---- |

4. Conclusions:
Films containing metal (Cr / Ni) layer and a-Si are deposited using electron beam evaporation at higher substrate temperatures. X-ray absorption spectra measured at Total Reflection and higher angles to study the local environment around metal at surface and inside the film. The EXAFS analysis is able to explain the diffusion of metal and formation of silicide at different temperatures. The metal silicides and their diffusion across the film promote the crystallizing of a-Si.

5. References:
[1] Fan J C C and Anderson H, *J. Appl. Phys.* **52**, 4003 (1981)
[2] Wang ZM, Wang JY, Jeurgens LPH and Mittemeijer EJ *Phys Rev Lett* **100**:125503(2008)
[3] Wang JY, He D, Zhao YH and Mittemeijer EJ, *Appl. Phys. Lett.*, **88**, 061910–11 (2006)
[4] Mohiddon MA, Naidu KL, Krishna MG, Dalba G and Rocca F, *Phys. Status Solidi C* **9**, 1493-1995 (2012)
[5] Pascarelli S, Boscherini F, D’Acapito F, Hrdy J, Meneghini C, and S. Mobilio, *J. Synchrotron Radiat.* **3**, 147 (1996)
[6] D’Acapito F, Milita S., Satta A. and Colombo L., *J. of Appl Physics* **102**, 043524 (2007)
[7] Newville M, *J. Synchrotron Radiat.* **8**, 322 (2001)
[8] Raveland B. M. Newville, *J. Synchrotron Radiat.* **12**, 537 (2005)
[9] Mohiddon M A, K Lakshun Naidu, Ghanashyam Krishna M, Dalba G and Rocca F, *in preparation* (2012)