Al Thermal Diffusion in *a*-$Si_{1-x}C_x$:H Thin Film Studied by XAFS

R.J. Prado[1], M.C.A. Fantini[2], M.N.P. Carreño[3], I. Pereyra[3] and A.M. Flank[4,5]

[1] *Depto. de Física / ICET / UFMT, Av. Fernando Corrêa s/n, Coxipó, CEP 78060-900 Cuiabá – MT, Brazil.*
[2] *Instituto de Física USP, C.P. 66318, CEP 05315-970, São Paulo – SP, Brazil.*
[3] *Escola Politécnica USP, PEE / LME, C.P. 8174, CEP 05508-970, São Paulo – SP, Brazil.*
[4] *CNRS-UR1 – SOLEIL – Gif sur Yvette – France*
[5] *Swiss Light Source – Villigen - Switzerland*

Abstract. In this work the local structure around the aluminium atoms, diffused by thermal annealing in *a*-SiC:H thin films was analyzed by x-ray absorption near edge structure (XANES), aiming to obtain information about the Al ordering after annealing. The thermal annealing of the films was performed in ultra high-vacuum (UHV), in order to avoid Al oxidation. The XANES spectra were obtained in-situ at the Al K-edge (1559 eV), immediately after the annealing process, showing that Al diffusion clearly takes place for carbon rich films. The theoretical simulation of these spectra shows that the Al in carbon rich *a*-SiC:H has structural order similar to that of c-Al_4C_3.

Keywords: PECVD; a-SiC:H; doping; XANES, Al_4C_3.
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INTRODUCTION

Theoretical and experimental studies on *n* and *p* doping of several silicon carbide crystalline polytypes are described in literature [1-3]. However, only few works about Al doping of a amorphous SiC phase (*a*-SiC:Al) or about the interface of *a*-SiC with Al were carried out [4,5].

Therefore, the aim of this work is to attain a better understanding about the low Al doping efficiency in *a*-$Si_{1-x}C_x$:H thin films. This kind of study may be the start-up for the development of an appropriate process of Al doping for the *a*-SiC:H, compatible with thin film technology processes.

EXPERIMENTAL

The *a*-SiC:H thin films were grown by Plasma Enhanced Chemical Vapor Deposition (PECVD) in special deposition conditions [6,7], in order to produce highly homogeneous films that do not present phase segregation for annealing temperature up to 1200 °C. The choice of a thermal diffusion process, instead of ion implantation, for the Al doping of the *a*-SiC:H films is justified by its low cost, better compatibility with the PECVD process and thin film technologies.

Al layers of 15 or 20 nm were deposited by e-beam onto the films. Inside the ultra high-vacuum (UHV) chamber ($10^{-9}/10^{-10}$ Torr) of the SA32 beamline (SuperACO ring) at LURE (Orsay, France). The samples were cleaned with a Ar^+ ion gun, annealed by electron bombardment and XANES measurements at the Si and Al K-edges were done. A KTP ($KTiOPO_4$) double crystal monochromator was used, and the XANES spectra were obtained by measuring the total drain current (TEY).

The FEFF8 code [8] was used to theoretically simulate the experimental spectra.

RESULTS AND DISCUSSION

The Al Annealing Onto (100) Si Substrates

Figure 1 shows the annealing of an Al layer deposited directly onto a single crystal (100) Si substrate. The formation of a shoulder at the edge and the increasing intensity of the peak at 1572 eV indicate that the Al layer oxidizes during annealing. The thermal treated sample returns to the original state, *i.e.*, metallic (100)Si/Al, after Ar^+ bombardment.

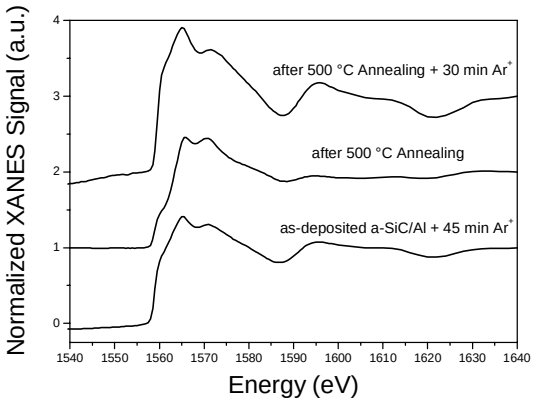

FIGURE 1. XANES spectra of 150 Å thick Al layer deposited directly onto (100) Si substrate (i) as-deposited and Ar^+ bombarded (red), (ii) annealed at 500 °C (green) and (iii) annealed at 500 °C and subsequently bombarded with Ar^+ (blue).

The results indicate that (i) there is no diffusion of the Al through the (100) Si substrate, or (ii) the Al diffuses into substrate as metal. Another extended conclusion is that no measurable doping occurs in crystalline silicon substrate. Similar results are obtained with silicon rich a-$Si_{1-x}C_x$:H samples.

The Al Annealing Onto Carbon Rich a-SiC

For a-$Si_{1-x}C_x$:H with x = 0.5 or carbon rich samples, the XANES spectra of the annealed a-SiC:H/Al sample show the formation of a very ordered phase, clearly different from metallic Al or an oxide phase, as shown in figure 2 for sample SiC7 (x = 0.63). This ordered phase is formed even for very low annealing temperatures, ranging from 400 to 600 °C.

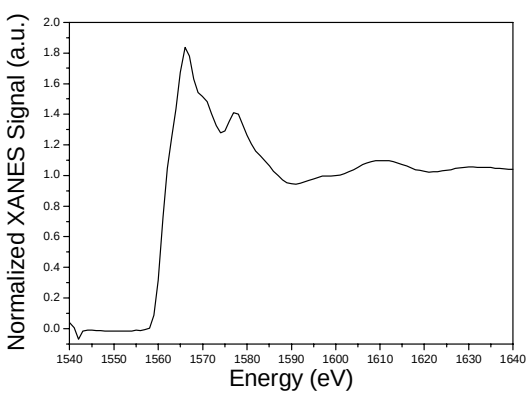

FIGURE 2. XANES spectra of a carbon rich sample SiC7 (c-Si/a-SiC/Al) after Al deposition, Ar^+ bombardment, and annealing at 450 °C.

One has to point out that no ordered phase of alumina is known to be formed after annealing at so low temperatures (T < 600 °C).

The Ar^+ Bombardment of the Annealed a-$Si_{1-x}C_x$/Al Samples

Whatever the duration of the Ar^+ bombardment (up to 285 minutes), the spectra of the annealed a-SiC/Al samples remain practically the same, as shown in figure 3, for sample SiC7 deposited onto UDAC (Ultra Dense Amorphous Carbon) substrate.

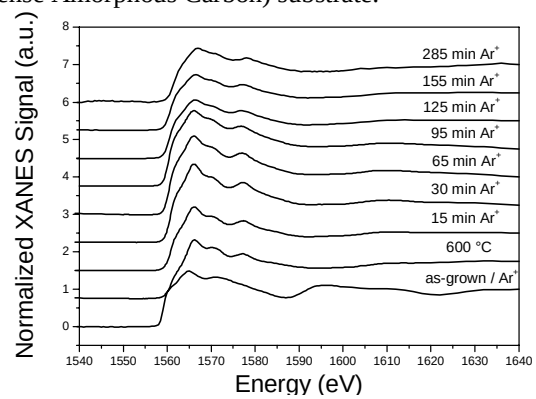

FIGURE 3. XANES spectra at the Al K edge for the SiC7 as-grown sample (UDAC/a-SiC/Al), after annealing at 600 °C and after several Ar^+ bombardment sessions.

The results in figure 3 show that the Al XANES signal is due to a phase almost homogeneously diffused in the a-SiC:H thin film, and not from the oxidation or modification of an Al superficial layer. The smaller intensities of peaks and other features found in the spectra after more than 125 minutes of Ar^+ bombardment are, probably, due to the smaller quantity of Al diffused deeply in the sample and, consequently, a more amorphous character of the Al_4C_3 phase found there. However, the main features remain in the spectra, at the same positions, besides their decreasing intensity, showing that the structural phase is more disordered, but similar to that found for more superficial layers.

Theoretical Simulations of the Structure

As input for FEFF8 calculations, four structures were used: two c-Al_3C_4 rhombohedal (R-32/m) structures [9,10] with bonding distances ranging from 0.189 to 0.224 nm; the theoretical β-AlC (similar to the β-SiC structure, with bonding distances of 0.189 nm); and the theoretical structure for an isolated Al atom replacing Si in β-SiC. As the first c-Al_4C_3 structure gives better simulation results, only the simulation of this structure is shown in this paper.

For the simulations shown here, the Hedin-Lundqvist exchange potential was used with an imaginary part of 0.5 eV to simulate the experimental broadening, a 70 atoms cluster to calculate the SCF

muffin-tin atomic potential, and a 120 atoms cluster for the FMS XANES calculation.

The structures of the aluminium oxides were not simulated due to the large literature data [11]. The experimental results revealed that the structural phases found in our work cannot be assigned to any of them.

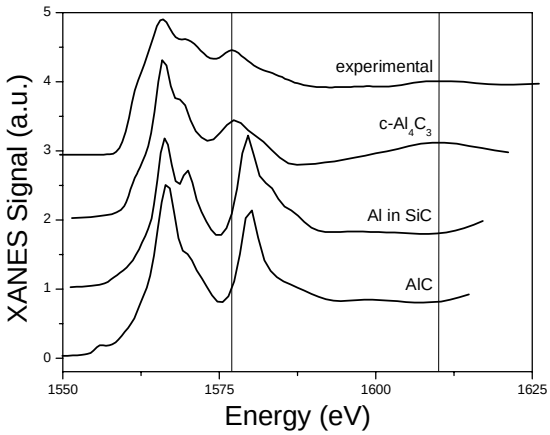

FIGURE 4. Experimental Al K-edge XANES spectra of a carbon rich sample after annealing and some simulations: (i) c-Al_4C_3, (ii) theoretical AlC structure, and (iii) one Al atom replacing Si in SiC.

Figure 4 presents The experimental spectrum compared to theoretical calculated spectra of different systems. The experimental data is very similar to those of c-Al_4C_3, which is the only data showing the large oscillation at 1610 eV and theoretical peaks at the same positions of the experimental ones.

The other spectra show more prominent peaks and features due to the higher crystalline symmetry of the cubic β-SiC structure used as initial model. In this structure the first neighbours are all at the same distance (0.189 nm) from the Al absorber. This is different from the rhombohedral c-Al_4C_3 structure, in which the first carbon neighbours are distributed from 0.189 to 0.224 nm.

The experimental peak at 1577 eV, a main contribution to the first shell of the experimental spectra, is in agreement with the position found for the theoretical Al_4C_3 structure. On the other hand, the first shell peaks of theoretically calculated AlC and Al in SiC phases, depicted on figure 4, are shifted to higher energy (1580 eV) compared to the experimental one. These results indicate that the first shell experimental distances are larger than those used for these simulations and, in a better accord to those used in the c-Al_4C_3 theoretical simulation.

In addition, the large oscillation at 1610 eV is reproduced only by the rhombohedral c-Al_4C_3 structure, definitely showing that this last structure better represents the experimental Al local structure inside the material studied in this work.

CONCLUSIONS

After annealing, there is no measurable formation of any Si/Al alloy, and only an Al_4C_3 phase was identified by XANES. Also, by XANES, there is not any evidence of thermal diffusion of Al in silicon rich *a*-SiC:H films and c-Si substrates, or the Al is diffused inside these systems as metallic clusters. However, it should be pointed out that doping levels in the order of parts per billion would be hardly detected by XANES.

In stoichiometric *a*-SiC:H and carbon rich thin films, the diffusion of the Al through the film thickness was successful, and a highly ordered Al_4C_3 phase is formed. The dominant presence of this phase, even at low annealing temperatures (ranging from 450 to 600 °C), explains the low *p*-type Al doping efficiency obtained until now for this kind of material.

The results obtained for stoichiometric and carbon rich samples indicate that the diffusion process is linked to the existence of carbon rich regions and/or pores in the material, through which Al can diffuse.

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REFERENCES

1. N.I. Kuznetsov *et al.*, Semiconductors **28**, 584-586 (1994).
2. A. Hallen *et al.*,in “Silicon Carbide and Related Mater. 1999”, Mat. Sci. Forum **338**, 869-872 (2000).
3. N.S. Saks *et al.*, J. Appl. Phys. **90**, 2796-2805 (2001).
4. B. Bian *et al.*, J. Phys. D–Appl. Phys. **25**, 871-874 (1992).
5. B. Bo *et al.*, Thin Solid Films **230**, 160-166 (1993).
6. R.J. Prado *et al.*, J. Non-Cryst. Sol. **283**, 1-10 (2001).
7. R.J. Prado *et al.*, J. Appl. Cryst. **34**, 465-472 (2001).
8. A.L. Ankudinov *et al.*, Phys. Rev. **B 58**, 7565-7576 (1998).
9. G.A. Jeffrey and Victor Y. Wu, Acta Cryst. 20, 538-547 (1966).
10. R.W.G. Wyckoff, *in* “Crystal Structures”. Wiley (1963).
11. Ph. Ildefonse, D. Cabaret, Ph. Sainctavit, G. Calas, A.M. Flank and P. Lagarde, Phys. Chem. Minerals **25**, 112-121 (1998).