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Aluminium and silicon determination on two Si–Al sputter targets used for magnetron sputtering

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Abstract

Si–Al coatings of different stoichiometry can be produced by unbalanced magnetron sputtering. The Si–Al alloy target used for this technique are prepared by two different ways:
- Silicon and aluminium are reduced to powder and pressed together in order to obtain a homogeneous target containing a known amount of aluminium and silicon.
- Si–Al alloy is produced by Péchiney (Voreppe, France) and contains small silicon grains impregnated into a Si–Al alloy.

Aluminium and silicon concentrations of such alloys were measured by Proton Induce X-ray Emission (PIXE) using the microprobe facility at LARN (Namur, Belgium). Measurements were carried out in the tracks due to material removed by sputtering when the target is used for DC-magnetron and also in the virgin zone where no material has been removed.

The results show clearly that the relative concentrations of Al and Si are not preserved when the target is sputtered with 500 eV Ar atoms. This result can be explained by the different sputtering yields of Al and Si and the stoichiometry of the coatings are related to the composition of the target. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: PVD; Magnetron sputtering; Si_xAl_y; Coatings; Thin film; Microanalysis

1. Introduction

"Sialons" are phases in the Si–Al–O–N and related systems based on the $(Si,Al)(O,N)_4$ tetrahedral structure. They have several interesting mechanical, chemical and thermal properties to make them candidates for high temperature applications. In the past years, there has been increasing interest in the deposition of composite films to meet the scientific and technological requirements for new and innovative properties of coatings. Combining good properties of a relatively ductile or soft substrate easy to produce with relatively hard layers like ceramics is a challenge to realise functional work pieces with optimal surface properties.

Preliminary study on the characterisation of unbalanced magnetron sputtering Si–Al coatings

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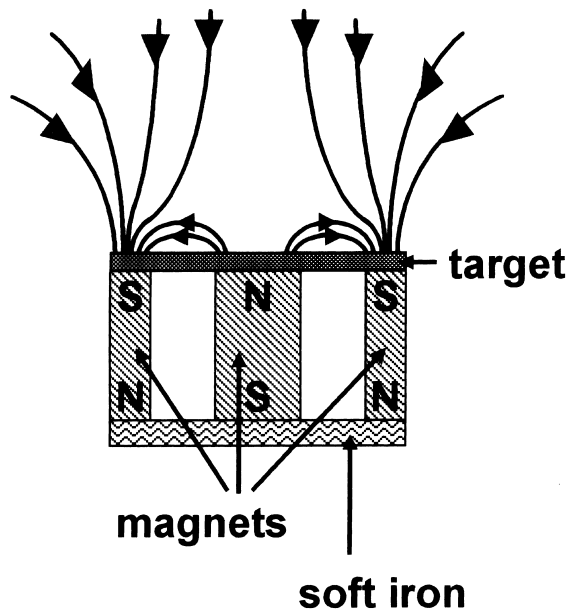
Fig. 1. Arrangement of the magnets in the cathode of the un-balanced DC-magnetron sputtering; the arrows indicate the magnetic field lines.

2. Preparation of coatings

The coatings were deposited using an unbalanced DC-magnetron sputtering system placed in a small chamber of 0.05 m^3 equipped with a 280 l/s turbo-molecular pump which provides a base pressure of 10^{-7} Torr. The sputtering target consists of 2 in. diameter disk and is placed just above the magnets with a good thermal contact in order to cool the magnetic material with water during deposition. The field lines of the cathode for this unbalanced DC-magnetron are shown in Fig. 1. This kind of magnetic arrangement provides a sputter track in the shape of a ring of about 3 cm diameter. A sputtering target bias voltage of -500 V was produced by a 500 W DC power supply.

Two different Si–Al alloys were used as sputter targets: the composition of the first target (T1) provided by Péchiney (Voreppe, France) is $Si_{50}Al_{50}$ and the second target (T2) provided by GfE (Augsburg, Germany) is made by pressed powder of aluminium and silicon with a composition of $Si_{70}Al_{30}$. Table 1 gives the nominal compositions as well as the expected compositions taking into account the sputtering yields of Al and Si and the type of the sputtering targets used. In order to measure the composition of the coatings made by using those cathodes, we have deposited a 200 nm Si–Al layer on glassy carbon. Rutherford Back-scattering spectroscopy (RBS) technique with 2 MeV α incident particles was used to measure the thickness and the composition of the coatings. A typical spectrum observed at a scattering angle of 175° is shown in Fig. 2. We can observe the surface contamination (O_{surf} and C_{surf}) as well as oxygen contamination between the Si–Al coating and the glassy carbon. The experimental data were simu-

has already been published [1]. In this work we have studied the experimental conditions and the properties of thin Si–Al films produced by unbalanced DC-magnetron sputtering, which will be used for further N_2^+ and O_2^+ implantation in order to produce thin "Sialons" coatings with specific properties [2]. Knowing the composition of the sputtering target is essential to obtain coatings with a desired stoichiometry. Two different Si_xAl_y targets with a composition of $Si_{50}Al_{50}$ and $Si_{70}Al_{30}$ were used. The composition and the deposition rates of the coatings produced depend on the structure of the sputter target.

Table 1
Description of the sputter targets used. The nominal composition is the composition given by the supplier, the expected composition has been calculated taking into account the sputtering yields of Si and Al and the measured composition has been obtained by RBS spectroscopy on the coatings prepared with the targets

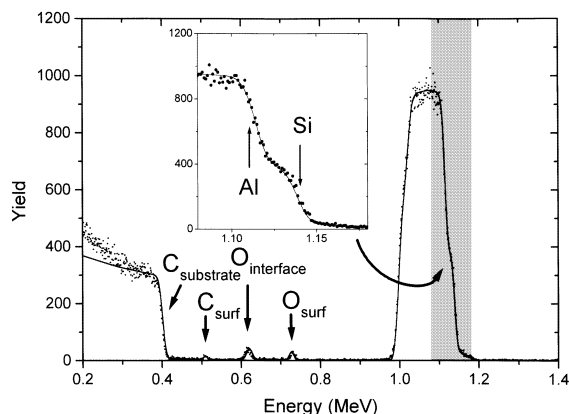| Target number	Nominal target composition	Expected film composition	Measured film composition	Film thickness (10^{15} at/cm^2)	Description target
T1	$Si_{50}Al_{50}$	$Si_{33}Al_{67}$	$Si_{38}Al_{62}$	1380	Si grains in Al matrix
T2	$Si_{70}Al_{30}$	$Si_{54}Al_{46}$	$Si_{63}Al_{37}$	1070	Pressed powder

Fig. 2. Experimental (●) and simulated (─) RBS spectrum measured with 2.0 MeV α-particles detected at 175° for a typical Si–Al coating deposited by unbalanced DC-magnetron sputtering on a glassy carbon substrate.

lated by using RUMP code [3] and the solid line represents the simulated curve. The signals corresponding to Si and Al cannot be resolved due to the fact that the atomic masses of silicon and aluminium are too close but it is possible to measure silicon contents by fitting the shoulder at the right of the Al–Si peak (expanded figure). The thickness and the compositions of the Si–Al coatings obtained for 5 min deposition time are also presented in Table 1. A large difference between the expected composition and the measured composition can be observed, especially for the sputtering target T2.

3. Microanalysis of the sputter targets

Optical pictures of the sputtered area of both targets are shown in Fig. 3. The surfaces of the two sputter targets used are completely different. The roughness of the surface of the target T1 (Fig. 3a) is much greater than the roughness of the target made by pressed powder of aluminium and silicon (Fig. 3b). The dark lines in Fig. 3a are due to silicon grains oriented perpendicular to the surface while the area between Si grains correspond to holes where aluminium is located.

In order to explain the disagreement between the expected and the measured composition of the coatings, we have performed microanalysis by

PIXE inside and outside the sputtered track on both sputter targets. The 2 MeV proton beam produced with the 2.5 MV Van de Graaff accelerator was focused to a 15×15 μm^2 size by using the LARN microprobe facility. X-rays emitted by the targets were detected in a Si(Li) detector placed at 135° in the vertical plane containing the incident beam. A small collimator (500 μm diameter) was placed in front of the detector in order to decrease the count rate in the Si(Li) detector. The maximum dead time admitted during the measurements was 1%. The resolution of the detector, better than 170 eV, was smaller than the difference between the $K\alpha_{12}$ lines of Al and Si. In order avoid interference between Al and Si signals, the two regions of interest have been chosen at the left part of the Al $K\alpha_{12}$ line for aluminium mapping (light grey in Fig. 4) and at the right part of the Si $K\alpha_{12}$ line for silicon mapping (dark grey in Fig. 4).

Maps (200×1000 μm) of silicon and aluminium were recorded by steps of 20 μm in an non-eroded area and in the sputtered track of both targets. Cumulative X-ray spectra were also recorded during the mapping. Figs. 5 and 6 show the Al and Si maps in the respective sputtered areas for both targets T1 and T2. For both samples, aluminium and silicon are anti-correlated, especially for target T1, for which we have tried to determine the composition. X-ray spectra have been recorded for the same integrated current in the middle of a Si grain (dotted line spectrum in Fig. 4) and in the centre of an aluminium area (solid line spectrum in Fig. 4). For the silicon grain, 98.5% of the emitted X-rays are due to silicon, while 1.5% of the signal corresponds to aluminium. This small amount of aluminium observed is due to fluorescence caused by the $K\alpha_{12}$ and $K\beta_{12}$ lines of silicon, which are selectively absorbed by aluminium. The effect of fluorescence, simulated by using PIXBOY code [4], is of about 2% if we suppose that the proton micro-beam hit the target in a silicon grain located at 2 μm from an aluminium area. For the spectrum recorded in the middle of an aluminium area, $K\alpha_{12}$ X-ray lines from silicon are always observed and the ratio between Al and Si is 13.3 taking into account corrections due to the ionisation cross sections [5]. This means that the composition of those areas is probably the same as the eutectic
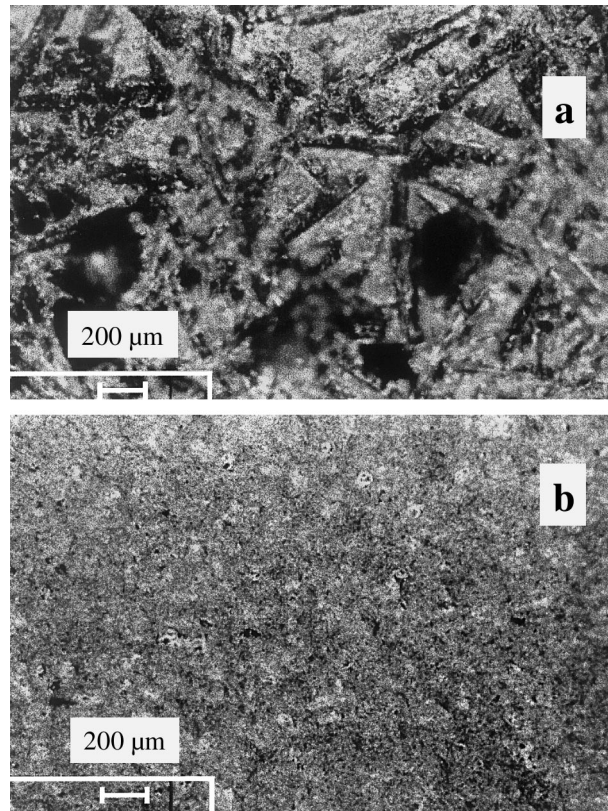
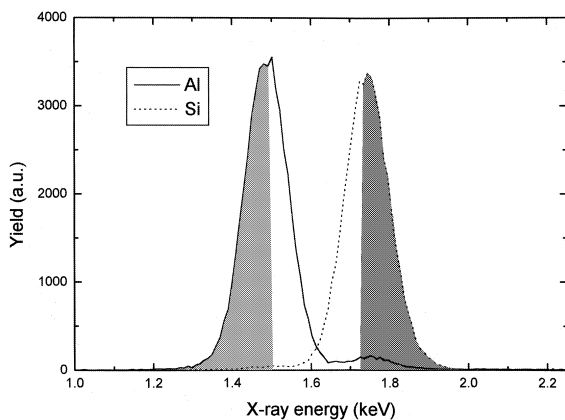Fig. 3. Optical picture of the sputtering tracks of the T1 (a) and T2 (b) targets.

Fig. 4. KX-rays observed on sputter target T1: the solid line spectrum corresponds to an impact in the middle of an aluminium area (light grey areas in Fig. 3a) and the dotted line spectrum is due to an impact in the centre of a silicon inclusion (dark grey lines in Fig. 3a).

alloy $Si_{12.6}Al_{87.4}$ [6]. Thus, the composition of the coatings prepared with target T1 is difficult to predict because we have also to take into account the difference in the sputtering yields of silicon and aluminium. For 500 eV Ar ions, the deposition rate for aluminium is twice the deposition rate for silicon because the ratio of the sputtering yields of aluminium and silicon is 2.1 (1.05/0.5) [7]. When target T1 is new, the composition of the surface is $Si_{50}Al_{50}$ and the stoichiometry of the coatings prepared is directly proportional to the sputtering yields of aluminium and silicon. The expected composition of the coatings should be around $Si_{33}Al_{67}$. When the erosion takes place, aluminium is preferentially sputtered and the surface of the target becomes poorer in aluminium. The roughness of the target is more and more important and edge effects take place so that it is impossible to predict the stoichiometry with such a target.
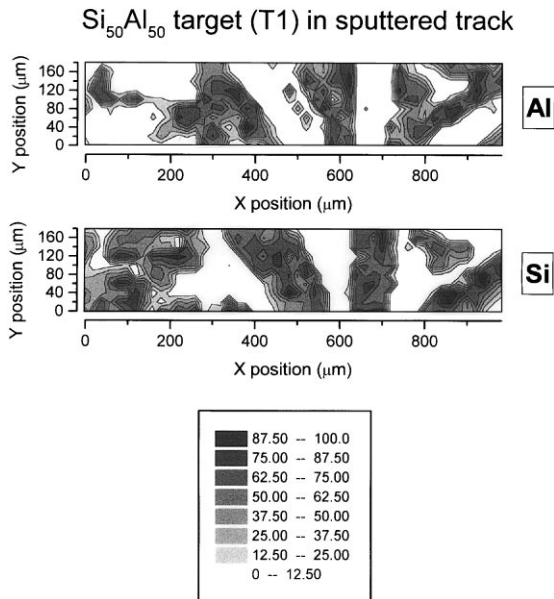
$Si_{50}Al_{50}$ target (T1) in sputtered track

Fig. 5. Aluminium and silicon maps of 200×1000 μm² observed on the sputter target T1. The steps are 20 μm and the different colours are related to the concentration of Si and Al.

$Si_{70}Al_{30}$ target (T2) in sputtered track

Fig. 6. Aluminium and silicon maps of 200×1000 μm² observed on the sputter target T2. The steps are 20 μm and the different colours are related to the concentration of Si and Al with the same colour scale as in Fig. 5.
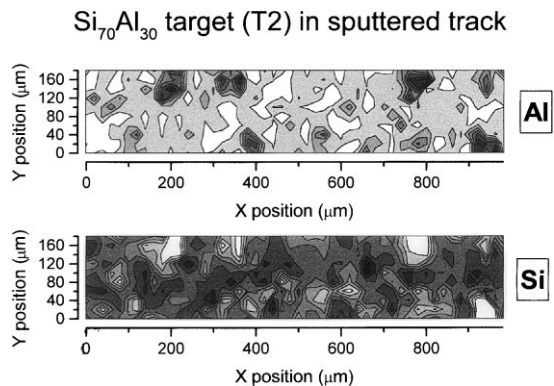
As explain above, we have recorded cumulative PIXE spectra during the mapping, for each area analysed. Fig. 7 shows the resulting spectra normalised to Si $K\alpha_{12}$ line. For both targets, the dotted spectra correspond to an irradiation in a virgin area of the sputter target, while the solid line
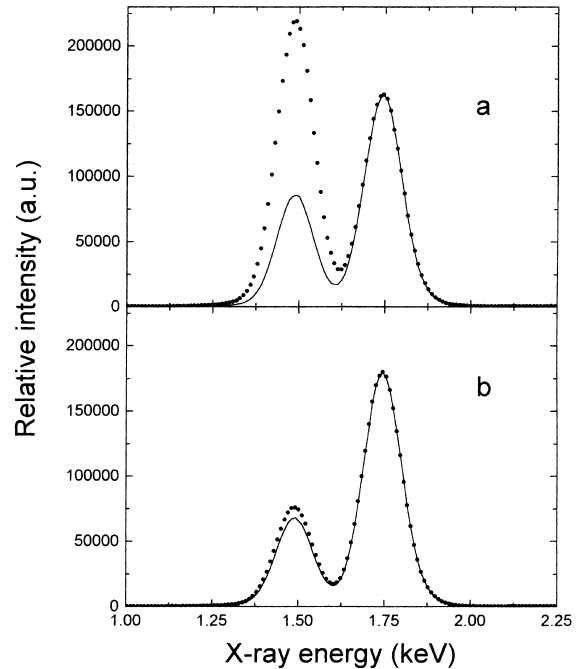

Fig. 7. Cumulative KX-ray spectra observed from sputter targets T1 (a) and T2 (b) during the mapping: the solid line spectra correspond to a mapping in the sputtered track while the dotted spectra are due to a mapping in a non eroded area of the targets.

spectra have been recorded in a sputtered track of the samples. A large difference between the intensity of the Al $K\alpha_{12}$ lines is observed for target T1 (Fig. 7a) and the relative ratios between Al and Si corrected for the ionisation cross sections [5] vary from 0.86 in a virgin area to 0.35 in the sputtered track. The results have not been corrected for fluorescence effect. This large difference is explained by the large roughness of the target. Aluminium is located in the holes between Si grains and Al X-rays are absorbed by silicon. The stoichiometry in the non-eroded area is $Si_{54}Al_{46}$, which is close to the nominal composition.

For the sputter target T2 the sizes of aluminium and silicon grains (<50 μm) and the roughness of the surface are smaller than for the previous target. Taking into account the sputtering yields of Al and Si, the expected composition should be $Si_{54}Al_{46}$ as indicated in Table 1. The difference between the expected and the measured composition is mainly

due to preferential sputtering of aluminium, which reduces also the Al concentration at the surface of the target. The cumulative X-ray spectra (Fig. 7b) are nearly the same in the non-eroded area and in the sputtered track and the ratio between Al and Si are 0.28 and 0.25, respectively. In the non-eroded area of target T2, the stoichoimetry of the target is $Si_{78}Al_{22}$ and if we calculate the expected composition of the coatings taking into account the sputtering yields, we obtain a stoichoimetry of $Si_{66}Al_{34}$ for the coatings prepared with this target. This stoichoimetry is close to the measured composition by RBS (Table 1). The same calculation done for the cumulative X-ray spectrum in the sputtered track gives $Si_{63}Al_{37}$, which is the same as the measured RBS value.

4. Conclusions

The thickness and the composition of the coatings prepared by using DC magnetron sputtering depend on the sputter target used because the sputtering yield of Al is approximately twice the sputtering yield of Si. During deposition, the surface of the sputter target is enriched with silicon and the measured composition of the coatings does not correspond to the initial composition of the sputter target. Due to preferential sputtering, aluminium is removed faster from the surface than silicon and the roughness of the sputter target is increasing. Microanalysis performed in the sputtered track of the target have shown that aluminium and silicon concentrations are anti-correlated but the composition of the target is very difficult to determine due to edge effect and absorption of the

Al $K\alpha_{12}$ X-rays by silicon grains, especially for the SiAl alloy provided by Péchiney.

We have also measured the composition of the pressed powder target (T2) by PIXE microanalysis technique during the mapping and the real composition is $Si_{78}Al_{22}$, which is quite different from the nominal composition ($Si_{70}Al_{30}$). The composition of the coatings deposited with this kind of sputter target should be $Si_{64}Al_{36}$ and is very close to the measured value ($Si_{63}Al_{37}$).

To avoid preferential sputtering effects, sputter targets machined with an assembly of Al and Si should be preferred to Si–Al alloys.

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