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Unbalanced magnetron sputtered Si–Al coatings: plasma conditions and film properties versus sample bias voltage

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Abstract

In this paper we present the results for 100–200 nm Si–Al coatings of different stoichiometry, produced by unbalanced magnetron sputtering, deposited on glassy carbon substrates with different Si_xAl_y target source compositions varying from pure aluminium to pure silicon and for substrate bias voltage ranging from 0 to −100 V.

The structure of the coatings has been analysed with cross-section transmission electron microscopy (TEM) and X-ray diffraction (XRD), while the composition and thickness were measured by Rutherford backscattering spectroscopy (RBS).

Cross-sectional TEM shows columnar growth, perpendicular to the surface of the substrate. The width of aluminium and silicon peak diffraction patterns indicates that all films containing both elements are composed of separated silicon and aluminium phases. The aluminium grains are bigger than the silicon ones and the dimension of the silicon grains decreases when the silicon concentration increases. When bias voltage is applied to the substrates, a contamination of argon is observed. On the contrary, no argon contamination is observed in pure aluminium films for all grounded coatings. The maximum argon concentration appears for bias voltages around −30 V and is proportional to the plasma ion density, which depends on the target composition. At lower bias voltages the argon concentration decreases and stays nearly constant below −60 V. The presence and the concentration of argon is correlated to heating of the substrate due to the impinging ions and electrons. © 1999 Elsevier Science S.A. All rights reserved.

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

1. Introduction

'Sialons' are phases in the Si–Al–O–N and related system 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 past years, there has been increasing interest in the deposition of composite films to meet the scientific and technological requirements for new and innovative coating properties. The aim is to combine the good properties of a relatively ductile or soft substrate, easy to produce, with relatively hard layers like hard ceramics to produce functional work pieces with optimal surface properties.

Preliminary study of the characterisation of unbalanced magnetron sputtering Si–Al coatings 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, which will be used for further N_2^+ and O_2^+ implantation in order to produce thin 'Sialons' coatings with specific properties [2]. Different sputtering Si_xAl_y targets with a composition varying from pure Al to pure Si were used. The composition, structure and deposition rates of the coatings produced by the different targets are discussed. We have also studied the composition, structure and temperature of the coatings when a negative bias voltage is applied to the sample holder.

2. Experimental details

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 turbomolecular pump which provides a base pressure of 10^{-7} Torr. A schematic view of the chamber is shown in Fig. 1(a). The

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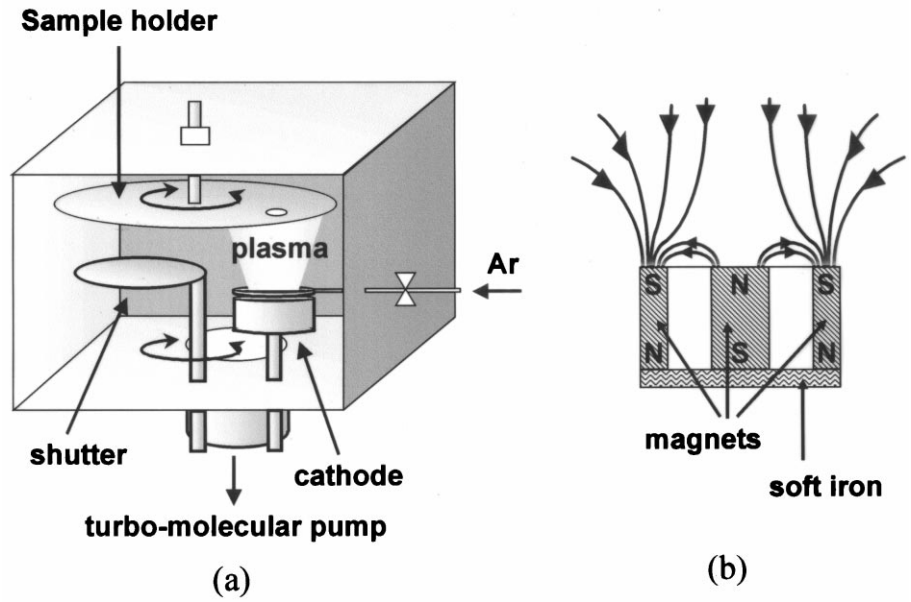

Fig. 1. (a) Schematic view of the unbalanced DC magnetron deposition chamber; (b) arrangement of the magnets in the cathode, the arrows indicate the field lines.

sputtering target consists of a 2-inch 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 this unbalanced DC magnetron are shown in Fig. 1(b). The characteristic self-bias voltage for this configuration can vary from −25 V to −33 V [3]. The sputtering target bias voltage was produced by a 500 W DC power supply.

Six kinds of composite sputtering target were used in order to cover a wide range of concentrations of silicon and aluminium for the samples. Pure aluminium (T1) and silicon (T2) disks were used to determine the deposition rates of the pure elements. Moreover, two different Si–Al alloys were used: the composition of the first target (T3) provided by Péchiney (Voreppe, France) is $Si_{50}Al_{50}$ and the second target (T4) provided by GfE (Augsburg, Germany) is made from pressed powder of aluminium and silicon with a composition of $Si_{70}Al_{30}$. Targets T5 and T6 consist of home-made 2 in targets of aluminium with small disks of silicon placed where the sputtering track is more important. The expected composition for the home-made targets is calculated by taking into account the relative area of Si and Al in the sputtered track, and also the sputtering yield of Si and Al, which is respectively 0.5 and 1.05 for 500 eV argon ions [4]. Table 1 gives the expected composition and the description of the sputtering targets used.

The Si–Al coatings were deposited on glassy carbon at a pressure of 2.4 mTorr controlled by an argon mass flow meter. The magnetron power was set to 140 W during deposition and the voltage applied to the sputtering target was around −500 V. Prior to deposition, each target was conditioned by sputtering for about 5 min with a shutter covering the source. The specimens were placed directly below the centre of the sputtering target, in line with the intense region of the plasma from the unbalanced magnetron. The source to substrate distance was 70 mm. The deposition time was 5 min in order to obtain a thickness of about 200 nm for the coatings. The substrate temperature was measured below 50°C during deposition with a thermocouple fixed at the rear of the substrate. A bias voltage can be applied to the sample holder and the specimens were realised at different polarisation ranging from 0 V to −100 V.

Table 1
Description of the sputtering targets used and calculation of the expected composition of Al and Si. The method used for determining the composition is explained in the text

Target number	Expected composition	Measured composition	Thickness (10^{15} at/cm^2)	Description
T1	Al_{100}	Al_{100}	1700	Pure metallic aluminium
T2	Si_{100}	Si_{100}	900	Silicon (111) (ACM, France)
T3	$Si_{50}Al_{50}$	$Si_{38}Al_{62}$	1380	Si–Al alloy (Péchiney, Voreppe, France)
T4	$Si_{70}Al_{30}$	$Si_{63}Al_{37}$	1070	Pressed powder (GfE, Augsburg, Germany)
T5	$Si_{28}Al_{72}$	$Si_{29}Al_{71}$	1290	Metallic aluminium with 2 disk of silicon (20 mm)
T6	$Si_{16}Al_{84}$	$Si_{12}Al_{88}$	1530	Metallic aluminium with 2 disk of silicon (12 mm)

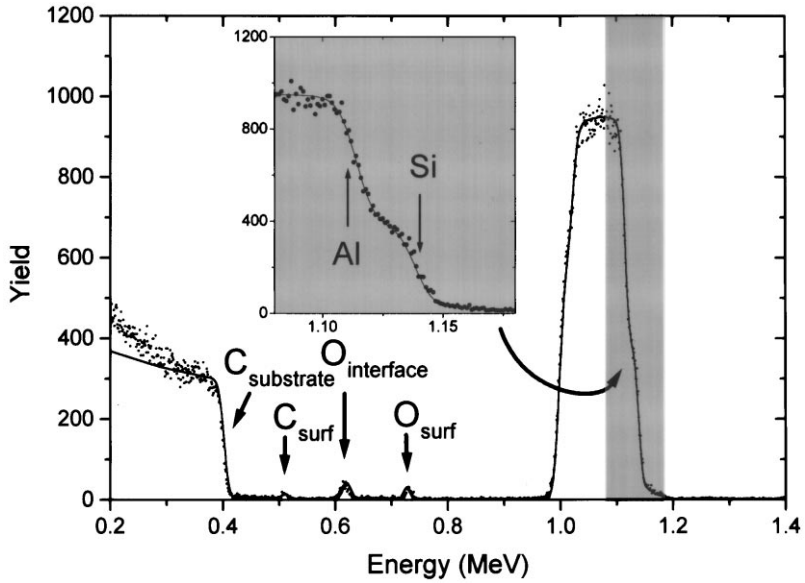

Fig. 2. Experimental (●) and simulated (—) RBS spectrum obtained with 2.0 MeV α-particles detected at 175° for a typical Si–Al coating deposited by unbalanced DC magnetron on a glassy carbon substrate.

3. Experimental results

3.1. RBS measurements

The thickness and composition of the coatings were measured by Rutherford backscattering spectroscopy (RBS) technique with 2 MeV incident α-particles. A typical spectrum observed at a diffusion angle of 175° is shown in Fig. 2. The experimental data were simulated using RUMP code [5] and the solid line represents the simulated curve. The signals corresponding to Si and Al cannot be resolved due to the fact that 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 thicknesses of the Si–Al coatings are presented in Table 1. The deposition rate for aluminium target is 5.6×10^{15} at $cm^{-2}\,s^{-1}$, which corresponds to 9.4 Å s^{-1} if we assume that the density of Al in the coating is 2.7 g cm^{-3}. For the pure silicon target, the deposition rate is 3.0×10^{15} at $cm^{-2}\,s^{-1}$ and corresponds to 6.0 Å s^{-1} if we assume that the density of Si in the coating is 2.3 g cm^{-3}. We can observe that the deposition rate for aluminium is 1.9 times greater than the deposition rate for silicon, which can be directly related to the ratio between sputtering yield of aluminium and silicon

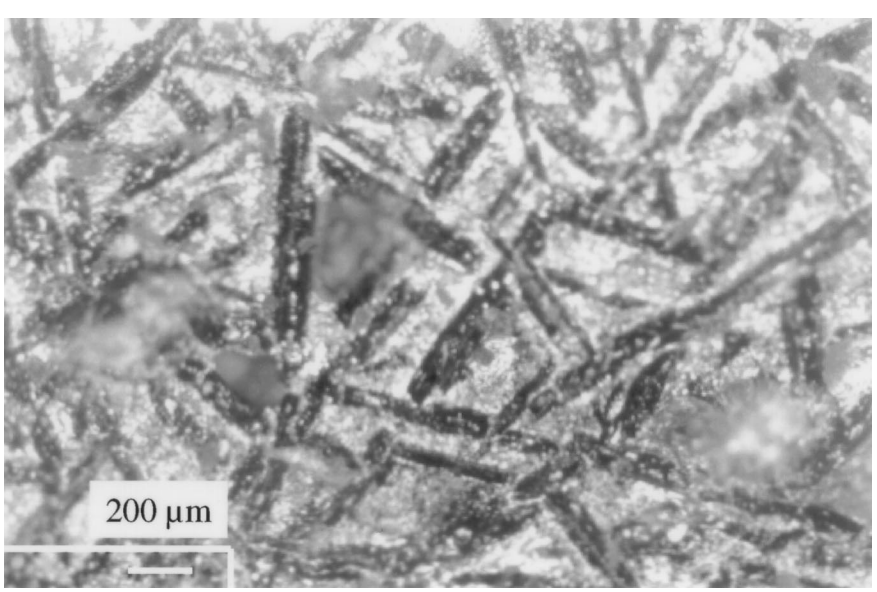

Fig. 3. Optical picture of the T4 target in the sputtering track.

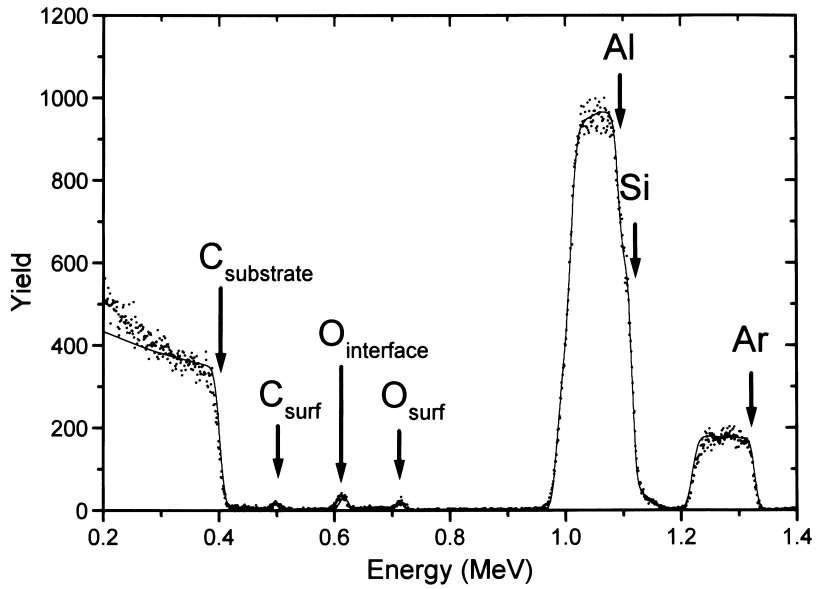

Fig. 4. Experimental (●) and simulated (—) RBS spectrum obtained with 2.0 MeV α-particles detected at 175° for a Si–Al coating deposited on glassy carbon by unbalanced DC magnetron with the sputter target T4. The bias voltage of the sample holder was set to −32 V.

(1.05/0.5 = 2.1) [4]. For sputtering targets T3 and T4, a large difference between the expected composition and the measured composition can be observed, especially for the sputtering target T3. This disagreement can be explained by preferential sputtering of aluminium: when one atom of silicon is removed from the surface of the target, two atoms of aluminium are removed. The picture in Fig. 3 shows the sputter target T3 where the erosion is more important. We can observe in the sputtered track some dark lines, which have been correlated to silicon and big holes (metallic grey) where aluminium is located. Microanalysis by PIXE in the sputtered track has been performed and shows clearly that the target becomes poorer in aluminium at the surface when material is removed [6]. This effect can be explained by the difference in sputtering yield between aluminium and silicon.

We have also studied the argon contamination versus bias voltage applied to the sample holder. Fig. 4 shows a typical RBS spectrum observed for the sputtering target T4 when the potential applied to the sample is −32 V. A huge contamination of argon appears in the whole Si–Al coating. The experimental data have been simulated using RUMP code [5] and the concentration of argon reaches 10 at% for the T4 sputter target (Fig. 5). When we plot the argon concentration versus the applied voltage of the sample, a narrow peak appears between −25 V and −40 V and the maximum concentration of argon increases with silicon contents of the sputtering target. Below −40 V, the argon concentration decreases rapidly and remains constant for voltage lower than −60 V.

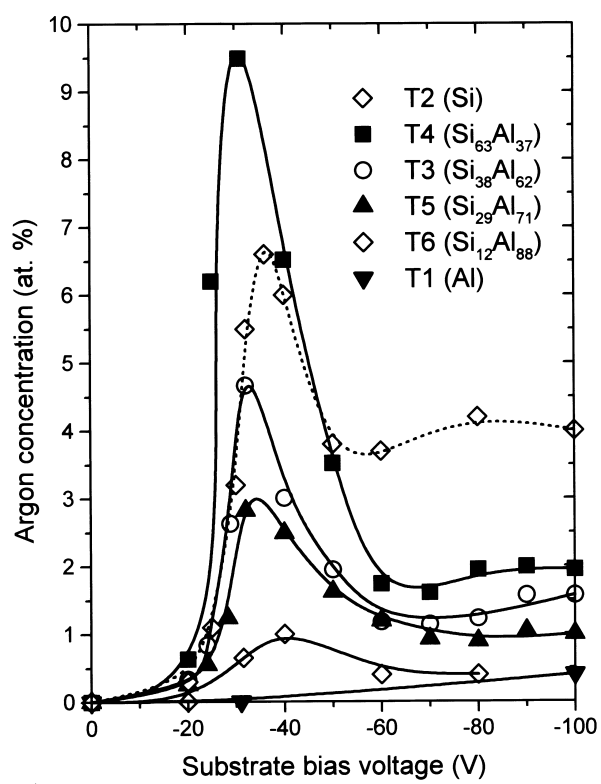

Fig. 5. Argon concentration obtained by RBS technique versus bias voltage of the sample holder.

3.2. XRD measurements

Glancing angle X-ray diffraction (GXRD) was carried out using a Philips diffractometer with Co Kα

radiation. The incident angle was 2°, which corresponds to an analysed depth of 2 μm. In order to obtain enough signal from the films, special coatings of 0.5 μm or 1 μm thickness were prepared on glassy carbon for GXRD measurements. The spectra obtained by this technique are presented in Fig. 6 for sputtering targets T3 to T5 under different bias voltages of the sample holder (0 V, −32 V and −80 V). The theoretical angle positions of the peaks due to carbon, aluminium and silicon are indicated on the figure. The wide peaks are due to the substrate of the coatings, which is glassy carbon. For all targets, peaks due to silicon are not visible and are probably lost in the background. For targets T3 and T5, the width of the peak at 45° due to aluminium decreases when the applied voltage is increased in absolute value. For target T4, almost no aluminium can be observed when the bias voltage is 0 V or −32 V. A small contribution of aluminium can be observed for the bias voltage −80 V.

3.3. Temperature of the specimen

The temperature of the specimen during deposition can be affected by the bias supply of the sample. In order to study the influence of temperature, special coatings were realised without cooling the substrate. We have measured the temperature of the specimen during deposition time of 10 min. The results are presented in Fig. 7 for different bias voltages. All curves have the same shape, except the curve relative to a substrate bias voltage of −20 V. The temperature is at first proportional to the deposition time and saturates more rapidly than the other curves. For the bias voltage ranging from 0 V to −10 V, the substrate temperature increases rapidly at low deposition times and saturates after 10 min of deposition. At bias voltage around −28 V the temperature increases slowly and reaches 100°C for 10 min deposition time. For lower substrate bias voltages (< −40 V), the increase in temperature is proportional to the bias voltage.

4. Discussion

RBS results indicate that the deposition rates depend on silicon contents of the sputter target. For bias voltage around the self-bias, a large contamination of argon appears in the coatings (Fig. 5). A similar property has also been observed by Shedden et al. [7] for Al–Mg coatings. The authors explained that the coatings with

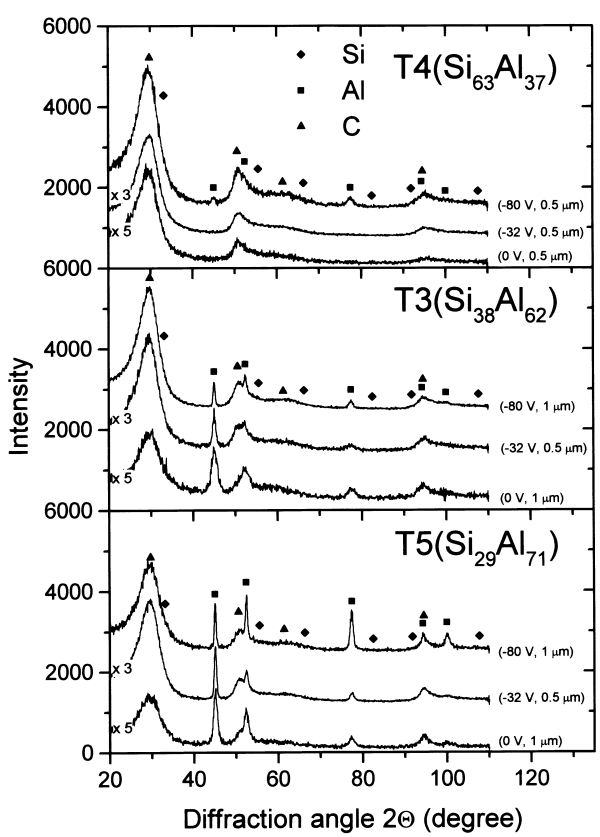

Fig. 6. GXRD spectra observed for the sputter target T3 to T5. The bias voltage of the sample holder was set to 0 V, −32 V and −80 V.

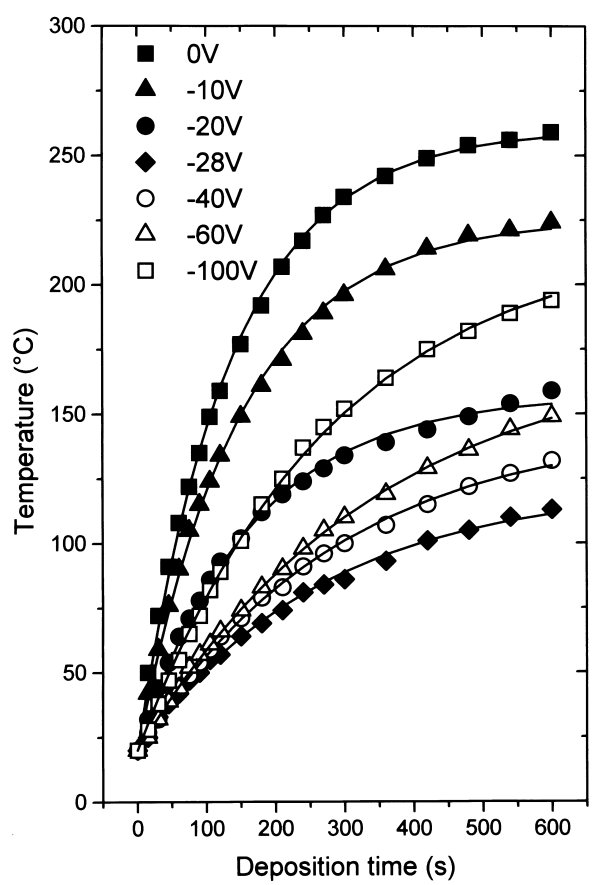

Fig. 7. Evolution of the substrate temperature versus deposition time for sample bias voltage ranging from 0 V to −100 V. The cathode used for the deposition was T3.

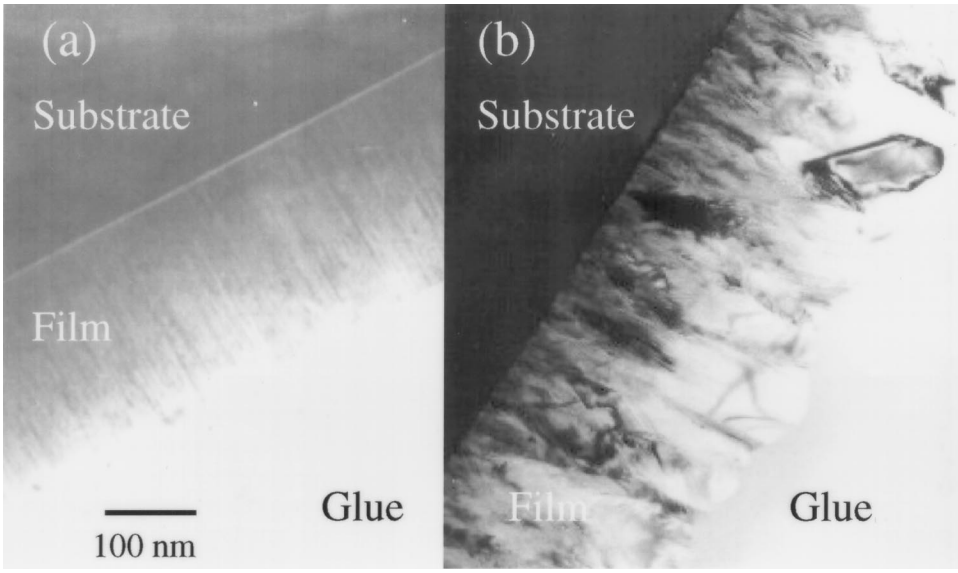

Fig. 8. Cross-sectional TEM pictures of the Si–Al coatings deposited with T4 cathode. The left picture (a) corresponds to a coating deposited with the self-bias voltage while the right one (b) was made with the sample holder connected to the earth.

high argon content are formed by an amorphous phase, which crystallises after room temperature ageing. We have measured by cross-sectional TEM two different specimens. Fig. 8(a) is a TEM picture of a Si–Al coating made with a self-bias applied to the sample holder while Fig. 8(b) corresponds to the sample holder connected to the earth. Both coatings were made using sputter target T4. The large amount of argon appears when small columns [Fig. 8(a)] form the coating structure, while large grains of Si–Al appear when the sample is connected to the earth during deposition [Fig. 8(b)]. With the Thornton diagram [8], which shows the structure of the coatings versus the temperature of the specimen and the partial pressure of Ar, this property can be explained because large grains in the coating are observed when the temperature of the specimen increases. If we plot the temperature of the sample measured after 5 min versus bias voltage, we can observe a minimum temperature for a bias voltage around -30 V (Fig. 9). From 0 to -20 V, the voltage difference between the plasma and the sample holder is so small that electrons can reach very easily the specimen; the temperature of the specimen is only produced by electron impact and decreases very rapidly when the bias voltage decreases. For sample bias voltages between –20 V and –40 V, Ar^+ atoms are accelerated to the specimen and trapped into the coating because the temperature of the specimen is low. For smaller bias voltage (< -40 V), the temperature of the specimen increases due to ionic implantation of Ar but electrons cannot reach the surface. When the temperature of the specimen increases, the size of the grains in the coating increases also, and less argon can be trapped into the layer. XRD measurements confirm this property. For samples T3 and T5,

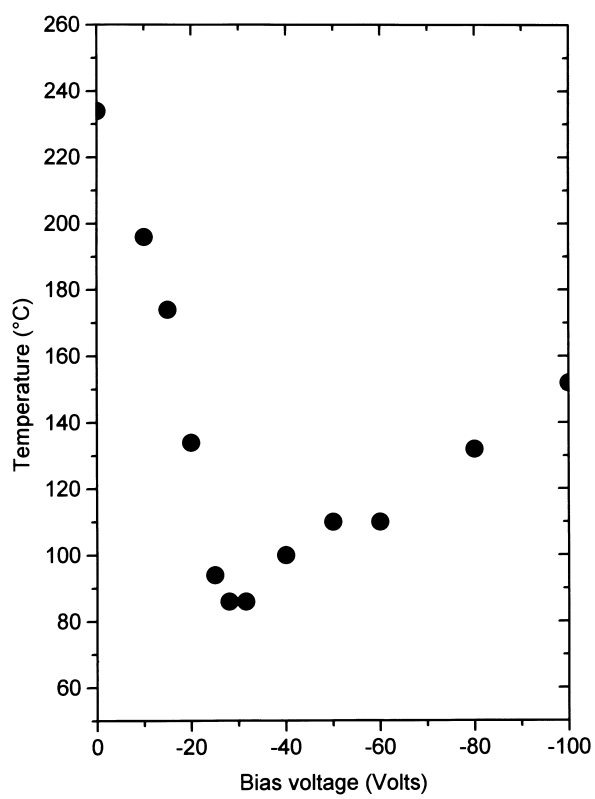

Fig. 9. Evolution of the substrate temperature versus sample bias voltage. The data were recorded after 5 min of deposition and are related to the measurements presented in Fig. 7.

the width of the peak due to aluminium at 45° decreases with the bias voltage of the sample holder, which means that crystalline Si–Al coatings are formed when the bias voltage of the specimen is lower than –40 V. An impor-

tant stress has also been observed for all specimens produced at self-bias potential.

5. Conclusions

The substrate bias voltage and the cathode design are important parameters for Si–Al coatings prepared by DC magnetron sputtering. The thickness and composition depend on the sputtering target used because the sputtering yield of Al is 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. Cathodes machined with an assembly of Al and Si should be preferred to Si–Al alloys.

Argon contamination in the coatings depends strongly on the bias voltage applied to the substrate holder. A maximum concentration of argon and smaller size grains growing in a columnar structure are observed when the bias voltage is around the self-bias. The lower temperature of the substrate explains this effect when self-bias voltage is applied to the sample holder.

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