SPUTTER CLEANING OF Al-BASED 5182 ALLOY STRIPS

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Abstract
Sputter cleaning is the most reliable way for the pre-treatment of substrates before the deposition of coatings with the aid of magnetron sputtering or vacuum arc deposition. The choice of a suitable technology for the sputter cleaning is critically important for the quality of further deposited layers, especially for their adhesion and corrosion resistance in case of a large area products. In this work a large-aperture (1400 mm) and high power (up to 10 kW) Hall discharge accelerator was developed for the sputter cleaning of large-area metallic substrates. The Hall accelerator developed is able to work with argon, oxygen, nitrogen and carbon dioxide. The maximum size of the treated strips is 2100×1300 mm. The current-voltage characteristic for oxigen is presented. The sputter cleaning of aluminum 5182 alloy strips has been characterized in terms of roughness and microhardness variation. The heating of the strip during sputter cleaning does not lead to a remarkable decrease of the hardness. The quality of an ionic etching was demonstrated with the aid of Auger electron spectroscopy.

Introduction

Ion beam processing has become an established method for surface treatment [1]. It includes techniques like sputtering, thin film deposition or ion implantation. Though the principle is the same in all cases [2], a given application requires a specific source design according to the ion energy range and uniformity needed. In the coating technology, substrate cleaning before coating is of particular importance for the quality of the further deposited layers, especially for their adhesion and corrosion resistance. Ion beam sputter cleaning proved to be an efficient method to produce high quality coatings on metallic, glass and polymeric strips. For sputtering purposes, Kaufman sources [3–5] are usually chosen. These sources are very attractive in the sense that a neutralized beam is generated with the ion energy, direction and current density independently controllable. The ion production is also separated from the substrate and target used. This high degree of control and beam uniformity make Kaufman sources very competitive towards plasma processes. However, inherent design considerations limit the use of such sources in production applications [6]. The source cathode and grid optics are critical components which require sometimes an excessive maintenance. The cathode, which emits electrons to ionize the discharge gas, is subjected to erosion due to sputtering by the ionized particles. Depending on the cathode type, the source lifetime ranges from a few hundred to one thousand of hours. Local heating or presence of active gases (such as oxygen) reduce dramatically the source lifetime by damaging the cathode. Grid optics, usually a screen grid and an accelerator grid are also subjected to erosion due to the space charge phenomenon or

due to the excessive ion beam current. This somehow limits the ion beam current that can be extracted from the chamber. In the coating applications, the source design must also meet the requirement of a large area treatment. In this work, a large aperture Hall current accelerator was developed for sputter cleaning of large area metallic, glass and polymer strips. Though less controllable than Kaufman sources, a Hall current accelerator appears better suited to sputter cleaning production requirements [5]. Of greater significance is the lack of any space charge flow limitation on ion current density.

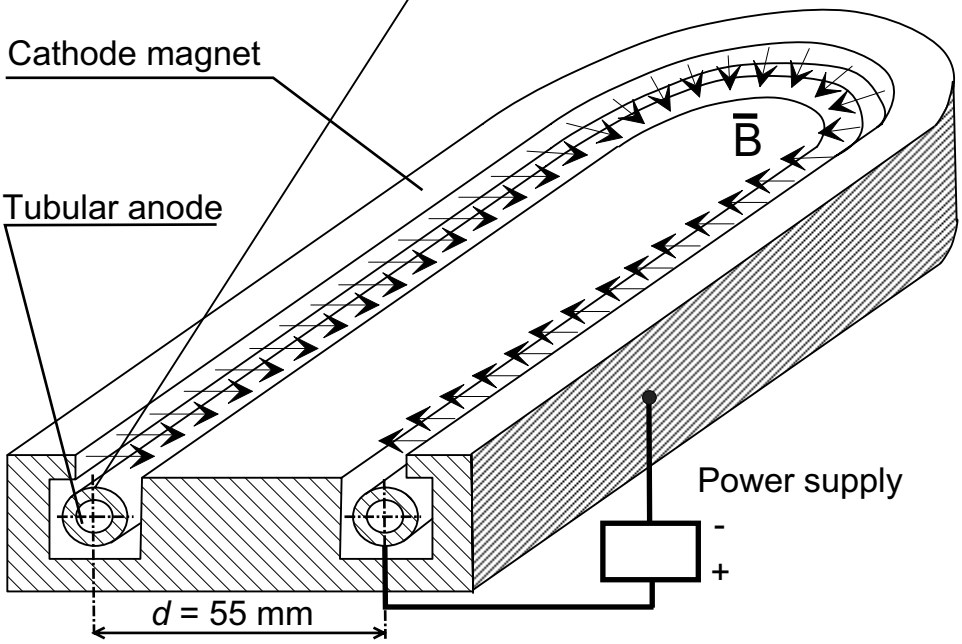

Figure 1. Scheme of the Hall current accelerator (half view through the middle plane)

Further, the reliability in etching is improved through the absence of any delicate structures like cathode or grid optics. The Hall current accelerator requires little maintenance and sputter cleaning can be performed with active gases such as oxygen, nitrogen and carbon dioxide.

Experimental

The scheme of the Hall current accelerator is shown in Figure 1 (half view through the middle plane). It has the shape of a very elongated loop. The Hall current accelerator described has a large aperture (1400 mm in the vertical direction) is used it in the multipurpose apparatus 'Nikolay' designed and construted in SONG Ltd. for deposition on large area metallic, glass and polymer strips by vacuum arc deposition and magnetron sputtering. Generally, such Hall current accelerator can be used in any apparatus with working vacuum better than 0.1 Pa. The aperture of the Hall current accelerator can be scaled up to 3000 mm without significant changes in design and, therefore, adjusted to a deposition apparatus. The maximum size of the treated strips in the apparatus 'Nikolay' is 2100×1300 mm. Strips to be treated are successively transported under the Hall discharge accelerator at a given translation speed, the substrate surface being perpendicular to the ionic flux axis. Changing this speed and accelerator power, one can control the sputter dose received by the substrate. The strip is then

immediately coated to prevent recontamination. The output capacity for glass is 30 strips in a production cycle (8 h). The source dimensions are 1400 mm in height with a twin aperture made of two slots, 55 mm away from one another. The Hall current accelerator consists of two juxtaposed permanent magnets which act as a cathode. Inside the groove made by the cathode, runs the water cooled anode of tubular shape. The whole construction is set under vacuum in the presence of a sputter gas (usually argon). The gas ionization and the subsequent ion acceleration is made through the presence of crossed electric and magnetic fields. The electric field is created by the cathode to anode potential drop whereas a quasi-uniform magnetic field is set between the two pole pieces of the cathode. In the presence of a low pressure gas and the electric field, a glow discharge plasma is initiated. The magnetic field traps the plasma electrons and together with the electric field, causes them to precess circumferentially along the anode surface. Through their cycloid path, they collide with argon atoms and ionize them.

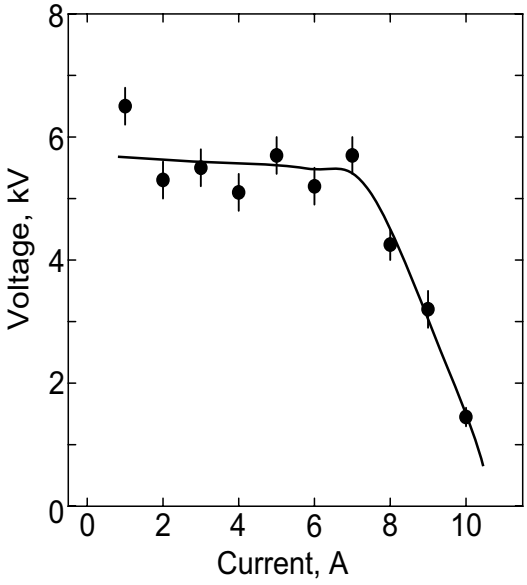

Figure 2. Current-voltage characteristic for oxygen at pressure of 3.8×10^{-2} Pa

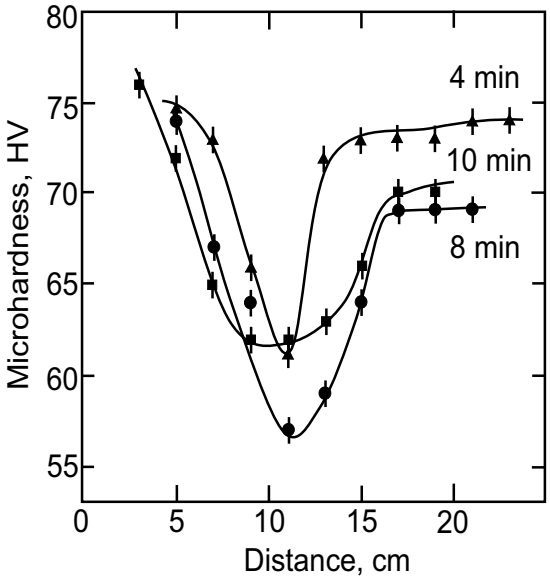

Figure 3. Microhardness of 5182 Al alloy after sputter cleaning. Minima correspond to the axis of the ionic source

The high difference of potential accelerates argon ions away from the anode and towards the substrate to be sputter cleaned. Usual values for the source power are 6 kV and 0.5 A under an argon pressure around 0.01 Pa. The resulting ion beam has an average energy of 6 keV. The current-voltage characteristic for oxigen at the pressure of 3.8×10^{-2} Pa is presented in Figure 2.

The source was characterized with aluminum samples. Cold rolled Pechiney 5182 Al alloy was used containing 4.65 wt.% Mg, 0.37 wt.% Mn, 0.03 wt.% Cu, 0.25 wt.% Fe, and 0.1 wt.% Si. In this study, the cleaning distribution was derived from microhardness measurements. 200×100×0.24 mm strips were sputter cleaned fixed to the source for different exposition times. Each sample was divided into ten smaller strips 20 mm wide. The initial microhardness was measured. After sputter cleaning, an average microhardness value was computed for each of the ten strips giving the profile of microhardness variation. Samples in both studies were placed 300 mm away from the source.

Cleaning of aluminium has been assessed in terms of impurity content after treatment. The influence of the cleaning dose and the sputter gas used on the impurity content was studied. The Al 5182 samples were cleaned at different doses and immediately coated with a thin TiO_2 film less than 300 nm thick. Two sputter gases have been used: oxigen and argon at a pressure of 1.5×10^{-2} Pa. The samples were placed in the industrial scale deposition apparatus 'Nikolay'. The cleaning conditions correspond for each gas to a maximum cleaning at low frame velocity (0.15 m/min), to medium cleaning at higher frame velocity (0.3 m/min) and no cleaning at all. The cleaning was performed through one return of the frame. The deposition parameters for the thin TiO_2 were the same for all samples: Ti was evaporated under a 2.4×10^{-2} Pa oxigen pressure. The frame velocity relative to the target was 3 m/min. Samples were then analysed using Auger electron spectroscopy (AES) in order to derive carbon content, considered as the main source of impurity. The specimens were mounted in the loadings of the spectrometer carrousel holder and sequentially rotated into the analysis position. The analysis was carried out with the excitation beam normal to the specimens. The spectra were taken during argon ion sputtering which produced a relatively clean surface of the sample under study without baking the system. The etching rate was considerably faster than the adsorption rate of the active residual gases. The Auger spectra were measured on a PHI-551 spectrometer with a double-pass cylindrical mirror analyzer. The base pressure was less than 2×10^{-8} Pa. The spectra were excited by an electron beam with an energy of 3 keV and a current of 8 μA through the sample. The peak-to-peak modulation was 3V. The sputtering was accomplished using a 5 keV Ar^+ ion beam. An ion gun was mounted to give a beam incidence angle of 70^o, and in order to minimize possible crater effects, it was rastered. The pressure of argon during sputtering was equal to 3×10^{-3} Pa. In order to provide a basis for comparison, a very pure aluminium polycrystal and a chemically cleaned 5182 aluminium samples were also analysed.

Results and discussion

Aluminum samples observation after treatment shows a change in the surface finish at the location of maximal sputtering. This 60 to 80 mm wide area is spotted by a light reflection change, the surface being less reflective in this central part. The roughness in this area is lower than on the edges. For a eight minutes sputter treatment, the roughness falls down from 400 to 250 nm. The cleaning provides a fine polishing of the surface. This application of sputtering is well known and has been already used for the finishing of optic glasses or the removal of scratches and surface strains after machining of metals [8–10]. For reasonable times (8 and 10 minutes), a very thin strip of aluminum looses its initial flatness and distorts itself due probably to the combined effect of substrate heating and relaxation of internal stresses by the partly removal of the superficial layer. Microhardness measurements show a maximal decrease in microhardness of about 40%. Increasing exposition time does not lower the microhardness but widen the area of ist maximal change as shown in Figure 3. For comparison, annealing of the 5182 aluminum alloy was done at different temperatures (200, 300 and 400°C) during 4 and 8 min. The measurements directly after treatment show a 30% decrease in the microhardness for samples annealed at 300 and 400°C. The samples annealed at 200°C did not encounter any change in the microhardness. This softening with temperature is related to the dissolution of α-phase precipitates. For an Al–5 wt.% Mg alloy, the dissolution occurs at 260°C which explains that no variation was measured for the samples annealed at 200°C [11]. Sputter cleaning of pure aluminum (99.999 wt.%) does not show any decrease in the microhardness. Annealed samples indicate that the microhardness variation is

mostly due to temperature elevation. The sputtering of the superficial layer induces a little change in the overall microhardness variation.

The AES data for the pure Al polycristal and the 5182 Al are show that at the surface of the samples, carbon contamination is high and decreases as we go deeper into the substrate. For large sputtering times, which correspond to the material bulk, the carbon content is still rather high (5 to 10 at. %) even for the very pure aluminium polycrystal. This may be explained by the surface finish of both samples. In the experimental set up the surface sputtering is accomplished using a 5 keV Ar^+ ion beam at the incidence angle of 70^o. The spectra is excited by an electron beam having an other incidence than the sputtering beam. The high surface roughness may provide some shadowing making the removal of all surface contamination impossible. The oxigen content shows also a surface contamination and some implantation in the neighboring. In the bulk of the material, oxigen content is equivalent to the carbon one. These preliminary spectra underline that without any treatment, the bulk of the 5182 aluminium contains around 5 at. % carbon which must be considered as the background content when reading the cleaning spectra. Figures 4 and 5 show respectively the resulting sample composition without any cleaning and with a maximal oxigen cleaning. The spectra show at the beginning, the presence of the thin TiO_2 film with some carbon content. The interface film/substrate is revealed by the sharp augmentation of Al content. In this region, the carbon atomic concentration increases in the case of the non cleaned sample while it decreases for the oxygen cleaned sample. In the bulk

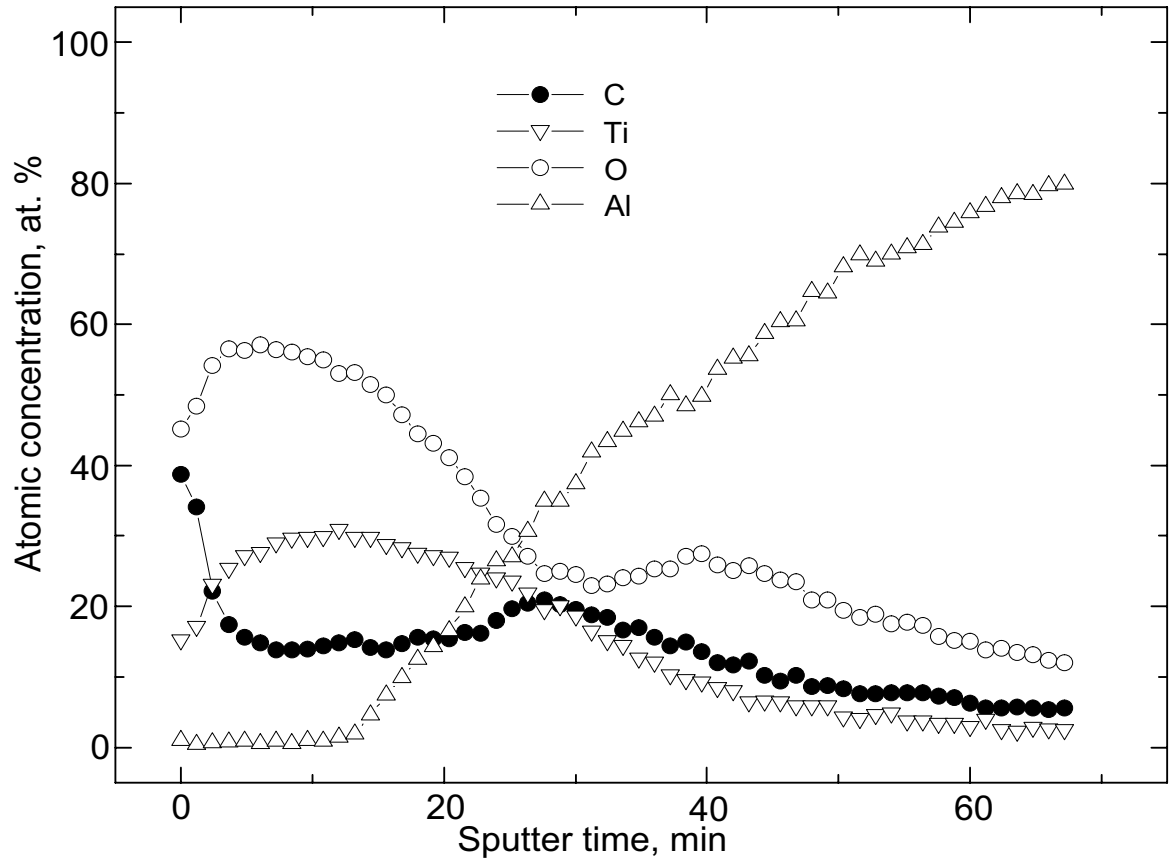

Figure 4. AES depth profile for the 5182 Al alloy coated with TiO_2 without preliminary cleaning

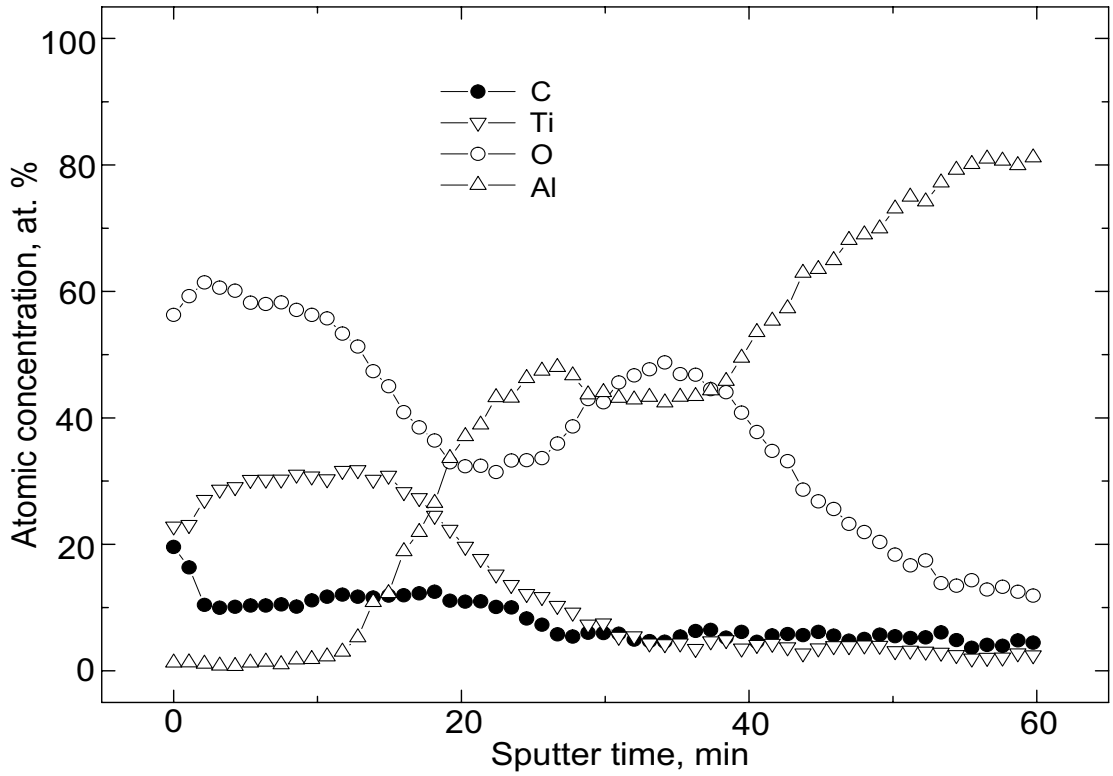

Figure 5. AES depth profile for the 5182 Al alloy coated with TiO_2 after maximal oxigen ionic sputter cleaning

the case of the non cleaned sample while it decreases for the oxigen cleaned sample. In the bulk of the material, a 5 at.% background content is found. The second noticeable cleaning effect is observed for the oxigen content. Sputtering induces implantation at the immediate neighbouring of the interface. It is revealed by the significative pick for oxigen after 30 min sputtering (Fig. 5). The same behavior is observed in the case of cleaning with argon. The carbon content pick at the interface disappears when sputtering is performed. However, no oxigen implantation occurs when sputtering with argon. Cleaning quantification with respect to the cleaning dose is rather hard to derive and no big difference is observed when the speed is increased by a factor of two.

Conclusions

A large aperture Hall current accelerator was presented. The absence of any lifetime critical components make it very attractive for industrial applications in comparison with Kaufman sources. Little or no maintenance is needed and active gases such as oxygen and nitrogen can be used for sputter cleaning. Sputter cleaning of Al alloy 5182 induces a polishing effect of the substrate surface and a 40 % decrease in the microhardness value. Increasing exposition time allows heat propagation towards the edges of the sample thus widening the area of microhardness variation without inducing a further decrease in the microhardness value. The Hall discharge accelerator enables to clean aluminium surface prior to coating. The influence of the sputtering gas is observed in the case of oxigen where some implantation occurs near the interface zone. The data on cleaning rate for silicate glass and poly(metil metacrylate) are published elsewhere [12].

Acknowledgements

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