Pre-treatment of large area strips with the aid of a high power Hall current accelerator

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Abstract

A large aperture Hall current accelerator has been developed for ionic cleaning of glass and metallic strips before vacuum arc deposition of protective and decorative layers. The accelerator has a large aperture of 1400 mm and power up to 10 kW. Various gases can be used for sputter cleaning: argon, nitrogen, oxygen, etc. The advantages of the Hall current source towards that of Kaufman in industrial processes are emphasized. The source sputter rates were measured. The maximal sputter rate is 7.5 nm/min for glass and 100 nm/min for poly(methyl metacrylate). The quality of ionic etching was demonstrated with the aid of Auger electron spectroscopy. The current–voltage characteristics for argon and oxygen are presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hall current accelerator; Ionic etching; Kaufman source; Sputter cleaning

1. Introduction

Ion beam processing is an established method for surface treatment [1]. It includes techniques like sputtering, thin film deposition and ion implantation. Though the principle is the same in all cases, a given application requires a specific source design according to the ion energy range and uniformity needed. By the coating of large substrates like glass sheets or steel strips for architectural and structural applications, the substrate cleaning before coating is of particular importance for the adhesion and corrosion resistance of the further deposited layers and, therefore, for the long-term stability of properties and of the appearance of coated parts in various environments. Ion beam sputter precleaning proved to be an efficient method to ensure high quality coatings on glass, metal and plastic sheets. For sputtering purposes, Kaufman sources [2–4] are usually chosen. These sources are very attractive in the sense that a neutralized beam is generated with independently controllable ion energy and current density. The ion production is also separated from the substrate and target used. However, inherent design considerations limit the use of such sources in production applications [5]. The source cathode and grid optics are critical components which sometimes require excessive maintenance. Local heating or presence of reactive gases (such as oxygen) dramatically reduce the source lifetime by damaging the cathode. Depending on the cathode type, the source lifetime ranges from a few hundred to one thousand hours. Grid optics of Kaufman sources limit the ion beam current that can be extracted from the chamber. In architectural and structural applications the source design must also meet the requirement of a large area treatment.

2. Experimental

In this work, a large aperture Hall current accelerator was developed for sputter cleaning of large area glass,

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metal and plastic sheets. Though less controllable than Kaufman sources, a Hall current accelerator appears better suited for sputter cleaning production requirements [4]. Of greater significance is the lack of any space charge flow limitation on the ion current density. Furthermore, 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 the sputter cleaning can be performed with reactive gases such as oxygen, nitrogen and carbon dioxide. The scheme of the Hall current accelerator is shown in Fig. 1. It has the shape of a very elongated loop. The large aperture (1400 mm in the vertical direction) allows one to use it in the multipurpose 'Nikolay' apparatus for deposition on large area glass and plastic sheets by vacuum arc deposition [6–8] and magnetron sputtering. Sheets 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 the speed and accelerator power, one can control the sputter dose received by the substrate. 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. A twin aperture has two slots, 55 mm away from one another. Two juxtaposed permanent magnets act as cathode. The water cooled anode of tubular shape runs inside the groove made by the cathode. The whole apparatus is set under vacuum in the presence of a sputter gas (usually argon). 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 an electric field, a glow discharge plasma is initiated. The magnetic field traps the plasma electrons and, together with the electric field, causes
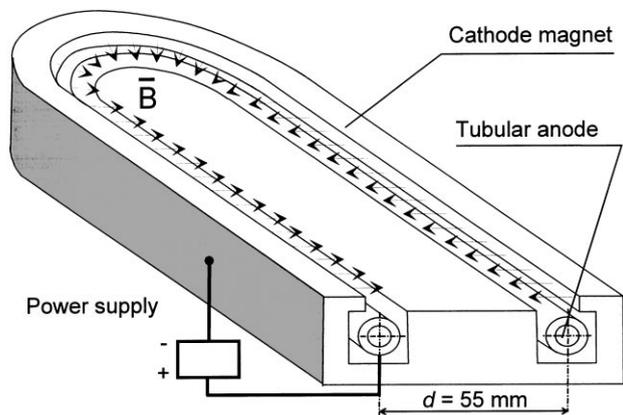
them to precess circumferentially along the anode surface. Through their cycloid path, they collide with argon atoms and ionize them. The high difference of potential accelerates the argon ions away from the anode and towards the substrate to be sputter cleaned.

In production of materials for architectural and structural needs, the sputter requirements are less demanding than in microelectronics or optics; nevertheless, the cleaning profile of the source must be known in order to estimate the sputter dose received by the substrates. A simple method was used to derive the source cleaning profile. Two hundred millimetre wide samples were sputter cleaned fixed to the source for different exposition times. Before cleaning, pen mark lines were drawn at a regular spacing interval on the sample surface. The pen marks provided masking against sputter cleaning of the sample surface. After cleaning treatment, they were removed with alcohol, leaving a step between the sputtered and non-sputtered parts. The step height was measured using a Taylor–Hobson profilometer. The measures along the width of the sample give the cleaning distribution of the source for a given exposition time. Such experiments were carried out on samples made of silicate glass and organic glass [poly(methyl metacrylate)]. The samples were placed 300 mm away from the source.

Cleaning of aluminium has been assessed in terms of impurity content after treatment. Al 5182 samples were sputter cleaned with oxygen at a pressure of 1.5×10^{-2} Pa at different doses and immediately coated with a thin TiO_2 film less than 300 nm thick. The samples were placed in the industrial scale deposition 'Nikolay' apparatus. The cleaning conditions correspond for each gas to a maximum cleaning at a 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 film were the same for all samples: Ti was evaporated under an oxygen pressure of 2.4×10^{-2} Pa. The samples were then analysed using Auger electron spectroscopy (AES) in order to derive the carbon content, considered to be the main source of impurity. 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 3 V. The sputtering was accomplished using a 5 keV Ar^+ ion beam. An ion gun was mounted to give a beam

Fig. 1. Hall current accelerator (section through the middle plane). The total length is 1400 mm.

incidence angle of 70° 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 chemically cleaned 5182 aluminium samples were also analysed.

3. Results and discussion

Cleaning profile for silicate glass is shown in Fig. 2. Similar profiles for an organic glass were published elsewhere [9]. As would be expected, the form of the profile depends on the material cleaned because silicate and organic glasses have a different behaviour towards sputtering. Silicate glass has a more reproducible cleaning profile with time in comparison to organic glass. Two distinct peaks appear in the distribution (Fig. 2). They correspond to two parallel parts of the elongated anode loop (Fig. 1). The twin construction of the source can thus be resolved in the cleaning profile of silicate glass. In the region of maximum sputter cleaning (corresponding to the two peaks), the sputter rate for glass almost reaches 7 nm/min. Organic glass has a lower thermal resistance compared to silicate glass. As a result, by sputtering longer than 5 min deterioration of the organic glass occurs. Below this value, the material is sputtered at a maximum rate of 100 nm/min [9]. The sputter cleaning of two materials of interest showed that the source cleaning profile is highly non-uniform and material dependent. The source profile for organic glass is difficult to interpret as the ion bombardment produces a combined effect of physical and thermal sputtering of the polymer with a low thermal resistance. Material deterioration similar to the damage induced by ionizing radiation can be expected [10].

The source cleaning profile for glass shows a distribution in agreement with the twin aperture source design. In a first approximation, the source profile can be modelled with a two-peak Gaussian profile distributi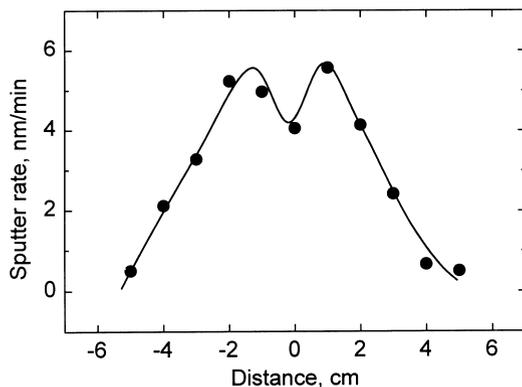on. Three hundred millimetres away from the source, the spacing between the Gaussian peaks (30 mm) is smaller than the distance d between the axes of the elongated parts of the anode loop (Fig. 1). This shows that the source beam is convergent and that a complete beam description would imply the derivation of the source cleaning profile for different distances from the source. As far as the process is concerned, silicate glass substrates, when cleaned, are moved relative to the source at a given translation speed. It ensures a uniform cleaning treatment over the glass panel surface. An estimation of the layer sputtered when moving at a given speed can be obtained by integrating the cleaning profile (expressed in cleaning rate units, e.g. nm/min) along the source width. For the speed range used in the industrial process, the silicate glass sputtered layer varies from 13 nm at low speed to 0.6 nm at high speed. At the most widely used speed, the thickness of the removed layer is 2 nm.

Usual values for the source power are the discharge voltage $U = 6$ kV and current $I = 0.5$ A under an argon pressure P of about 0.01 Pa. The resulting ion beam has an average energy of 6 keV. The current–voltage characteristic for argon at $P = 2.4 \times 10^{-2}$ Pa is presented in Fig. 3. At high voltages the current changes slowly. Below 3 kV the current starts to decrease, and the discharge becomes unstable. The parameters of discharge are rather independent of the method of gas input (into vacuum chamber or directly into Hall accelerator). The current–voltage characteristic for oxygen at $P = 3.8 \times 10^{-2}$ Pa is presented in Fig. 4. The interval of stable discharge is much broader in this case (discharge current up to 6 A). The measured current–voltage characteristics allow one to optimize the regime of sputter cleaning by finding the maximum power value at a stable discharge.

The AES depth profiles for the 5182 Al alloy without any precleaning (Fig. 5) and with maximal oxygen cleaning (Fig. 6) were measured. They show that at the surface of the samples, the carbon contamination is high

Fig. 2. Sputter profile for silicate glass. The line is a visual guide.
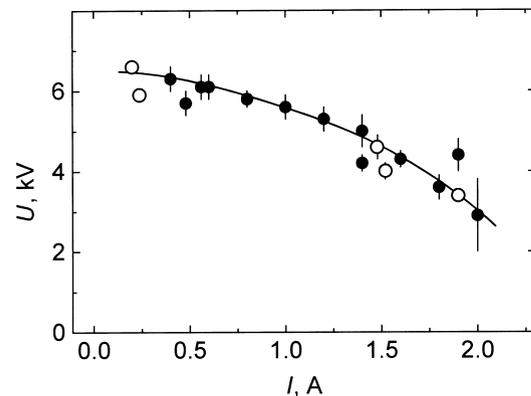
Fig. 3. Current–voltage characteristic for Ar at a pressure of 2.4×10^{-2} Pa. Gas input into the vacuum chamber (full symbols) and into the Hall accelerator (open symbols). The line is a visual guide.
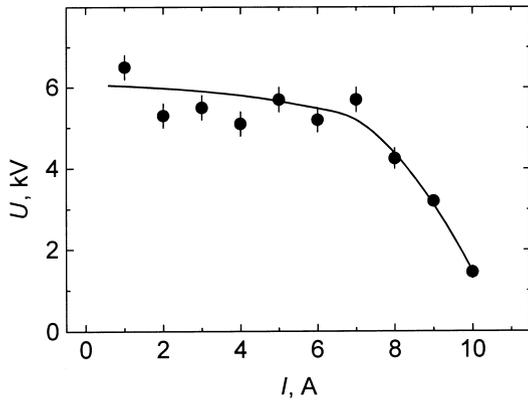
Fig. 4. Current–voltage characteristic for oxygen at a pressure of 3.8×10^{-2} Pa. The line is a visual guide.
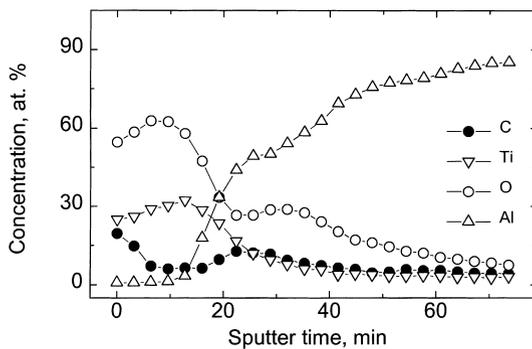

Fig. 5. AES depth profile for the 5182 Al alloy coated with TiO_2 without preliminary cleaning. The lines are visual guides.
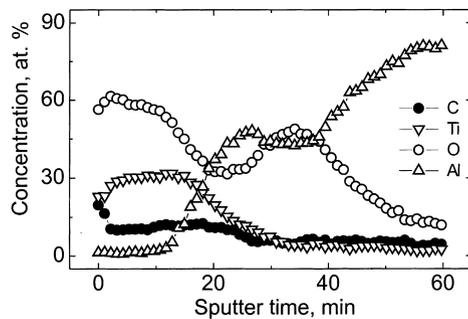

Fig. 6. AES depth profile for the 5182 Al alloy coated with TiO_2 after maximal oxygen ionic sputter cleaning. The lines are visual guides.

and decreases deeper into the substrate. For large sputtering times, which correspond to the material bulk, the values of carbon content is still rather high (5 to 10 at.%) even for the very pure 99.999 at.% Al 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 an incidence angle of 70°. The Auger electrons are 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 oxygen content also

shows a surface contamination and some implantation in the neighbourhood. In the bulk of the material, the oxygen 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. The spectra (Figs. 5 and 6) show at the beginning the presence of the thin TiO_2 film with some carbon content. The film/substrate interface is revealed by the sharp augmentation of the Al content. In this region, the carbon concentration increases in the case of the non-cleaned sample while it decreases for the oxygen cleaned sample. In the bulk of the material, a 5 at.% background content is found. The second noticeable cleaning effect is observed for the oxygen content. The sputtering induces implantation close to the interface. It is revealed by a significant peak for oxygen after 30 min sputtering (Fig. 6). The same behaviour is observed in the case of cleaning with argon. The carbon content peak at the interface disappears when the sputtering is performed. However, no oxygen implantation occurs by sputtering with argon.

4. Conclusions

A large aperture Hall current accelerator is presented. The absence of any lifetime critical components makes it very attractive for industrial applications in comparison to Kaufman sources. Little or no maintenance is needed, and active gases such as oxygen, carbon dioxide and nitrogen can be used for sputter cleaning. The source sputter profile under argon was determined for silicate glass and poly(methyl metacrylate) treated 300 mm away from the source. In both cases, the cleaning distribution is highly inhomogeneous and presents only a narrow area of maximal sputtering. Silicate glass has a cleaning rate about 12 times lower than that of poly(methyl metacrylate). The cleaning profiles are rather complicated, whereas for silicate glass the two-peak distribution induced by the twin aperture source can be resolved. This type of characterization enables one to give an estimate of the sputtered glass layer when the substrate is moved relative to the source at a given speed. The current–voltage characteristic measured for argon is presented. It allows one to optimize the regime of sputter cleaning by finding the maximum power value at a stable discharge. The quality of the sputter cleaning is demonstrated with the aid of AES depth profiling of uncleaned and cleaned Al alloy strip.

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