Pre-treatment of Large Area Glass Sheets

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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. In this work a large-aperture Hall current accelerator was developed for the sputter cleaning of large-area glass, metal and plastics sheets. The main advantage of the Hall current accelerator is the possibility to use reactive gases. The Hall accelerator developed is able to work with argon, oxygen, nitrogen and carbon dioxide. The accelerator has the form of a very elongated loop with a large aperture (1400 mm in the vertical direction). The maximum power of the Hall current accelerator is 10 kW. 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.

Introduction

For the past years, coating on glass has represented a growing market mainly due to the development in the field of architectural glass and electronics. It is now possible to design a multilayer coating which will fulfill a given criterion and leads to cost cuts. In architecture and automotive industry, the main developments are antireflective coatings for a maximal light transmittance and low emissivity coatings for thermal insulation. Complex multilayered coatings including conductive oxide or inorganic materials enable to create variable light transmission glass. A growing application is the "smart window" which regulates itself the light in a room. In addition to the complexity of the coating process, requirements such as thickness uniformity and defect minimalization are often needed on large areas. In order to achieve a high adhesion to the glass substrate, the contaminations must be effectively removed from the glass. All these restrictions strongly reduce the number of suitable cleaning techniques which should also achieve a high cleaning rate compatible with the feeding speed of the glass production lines. One of the most effective methods is the sputter cleaning of glass. The choice of a suitable technology for the sputter cleaning process is critically important, especially in case of large area products.

The main frame

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 glass coating technology, substrate cleaning before the 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 glass, metal and plastic sheets. 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 independently controllable ion energy and current density. The ion production is also separated from the substrate and target used. This high degree of control and beam uniformity makes Kaufman sources very competitive towards plasma processes. However, inherent design considerations limit the use of such sources in

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production applications [6]. The source cathode and grid optics are critical components which require sometimes an excessive maintenance. The cathode, which emits the 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 reactive 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 glass 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 glass, metal and plastic sheets. 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 the ion current density. 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 the sputter cleaning can be performed with reactive gases such as oxygen, nitrogen and carbon dioxide.

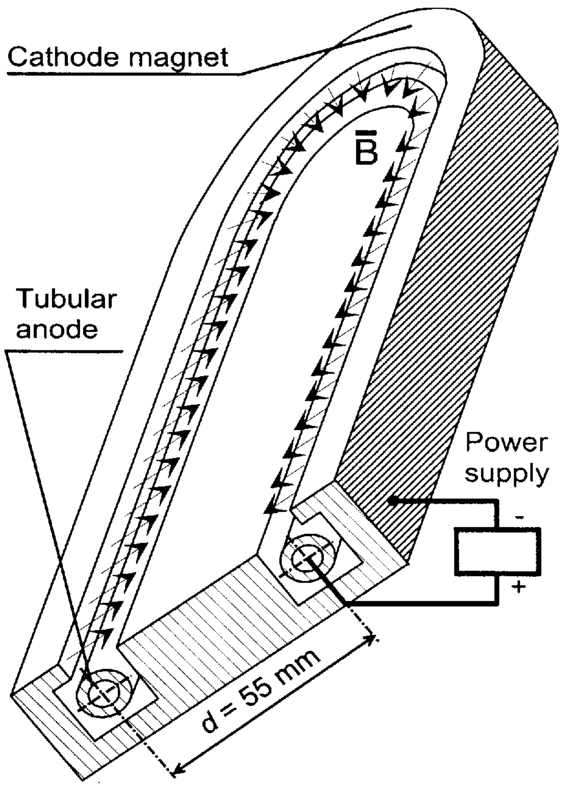

Figure 1. Scheme of a Hall current accelerator (section through the middle plane).The total length (aperture) is 1400 mm.

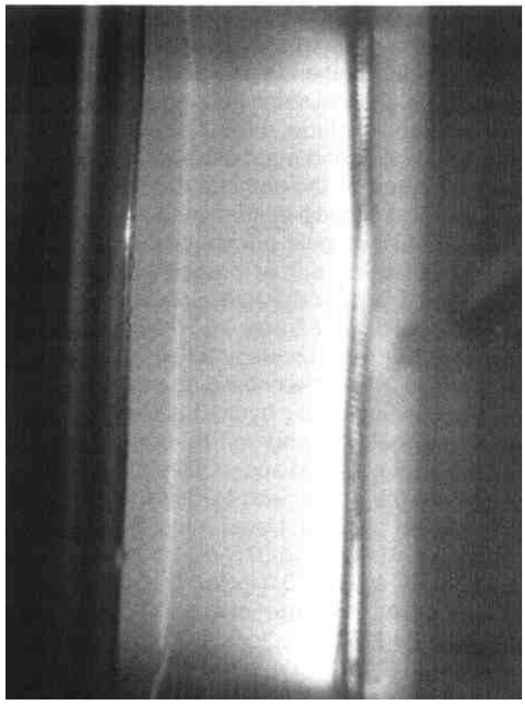

Figure 2. Hall current accelerator together with a glass sheet inside of the deposition facility. Only one source is working. The heated area on the glass surface is clearly seen.

The Hall current accelerator is shown in *Figure 1* (scheme) and *Figure 2* (photograph inside of the running deposition facility "Nikolay"). 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 apparatus "Nikolay" for deposition on large area glass and plastic sheets by vacuum arc deposition [7–9] and magnetron sputtering. The maximum size of the treated sheets is 2100mmx1300 mm. 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 (see Figure 2 where the parallel slots for the frames with glasses can be seen. The glass is positioned in the remotest left slot, only the right-hand source is running). Changing the speed and accelerator power, one can control the sputter dose received by the substrate. The sheet is then immediately coated to prevent recontamination. The output capacity for glass is 30 sheets in a production cycle. 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 cathode. Inside the groove made by the

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cathode, runs the anode of tubular shape and water cooled. The whole apparatus 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 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. Usual values for the source power are 6 kV and 0.5 A under an argon pressure of around 0.01 Pa. The resulting ion beam has an average energy of 6 keV. The current-voltage characteristic for argon at a pressure of 2.4×10^{-2} Pa is presented in *Figure 3*. It allows one to optimize the regime of sputter cleaning by finding the maximum power value at a stable discharge. At high voltages the current changes slowly. Below 3 kV the current starts to decrease, and the dicharge becomes unstable.

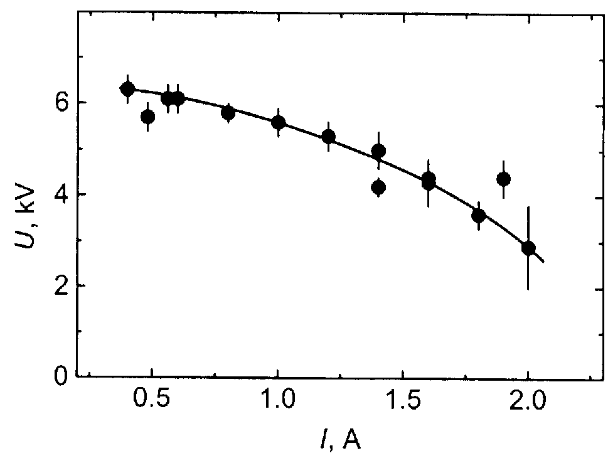

Figure 3. Current-voltage characteristic for argon at a pressure of 2.4×10^{-2} Pa. The line is a guide for the eye.

Therefore, a big progress is achieved since the early Hall current source of 10 cm aperture and ion beam energy of 50–75 eV was designed and fabricated [5]. It has been already quoted [4] that due to the unusual electron movement in Hall current accelerators, a greater energy spread, compared to Kaufman source, should be expected in the accelerated ion beam. The increased energy spread results from both charge exchange and plasma fluctuations.

Results

Though sputter requirements are less demanding in decorative glass industry than in microelectronics, the "cleaning profile" of the source has to be known in order to estimate the sputter dose received by the substrates. A simple method was used to derive the source cleaning profile. 200 mm wide samples were sputter cleaned fixed to the source for different exposition times. Before cleaning, pen marks lines were drawn at a regular spacing interval on the sample surface. The pen marks provide 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. Hence it gives conservative measures for the glass treatment as it corresponds to the furthest glass position from the source.

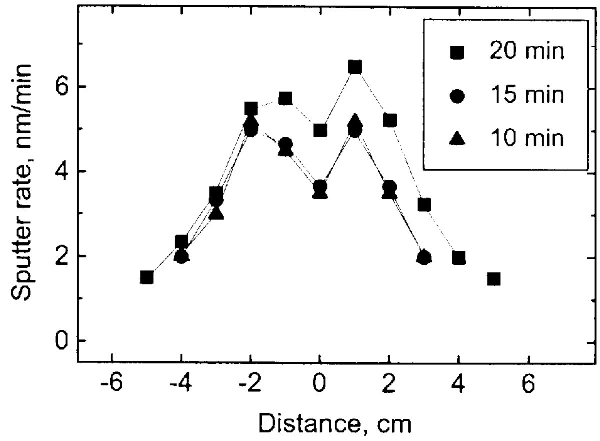

Figure 4. Sputter profiles for various sputter times (silicate glass). The lines are guides for the eye.

Cleaning profiles for silicate glass are shown in *Figure 4*. Similar profiles for an organic glass were published elsewhere [10]. As would be expected, the form of the profiles depends on the material cleaned because silicate and organic glasses have a different behaviour towards sputtering. Organic glass has a lower thermal resistance compared to silicate glass. Therefore, 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 [10]. Some reaction occurs with the sample as the surface is covered with a slightly brown

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layer. The cleaning process for organic glass seems to be a combination of physical sputtering and chemical deterioration.

Silicate glass has a more reproducible cleaning profile with time (Figure 4) in comparison with organic glass. The main difference is the appearance of two distinct peaks in the distribution. They correspond to two parallel parts of the elongated anode loop (see Figure 1). The twin construction of the source can hence 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. 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 [11].

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 distribution. 300 mm 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 (Figure 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.

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, 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.

Acknowledgements

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