Plasma Cleaning of Steel and Aluminium Studied by Optical Emission Spectroscopy and Langmuir Probe Measurements

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Argon sputter cleaning has been done on aluminium and stainless steel electrodes in an RF discharge. A time constant of 10 minutes was associated with the removal of water vapour as determined from the exponential decay of the optical signals from the OH and H radicals. A significant difference in the emission from H lines was found to depend on the choice of electrode material.
As the amount of water in the discharge was reduced, an increase in the emission intensity of the metal lines representing the composition of the surface was also observed. Only small changes were observed in the plasma parameters as a function of cleaning time. The electron temperature seemed to increase slightly, possibly due to a decrease in the hydrogen concentration in the discharge. The plasma potential and the floating potential were typically 6 volt higher when the electrode material was steel as compared to aluminium.

Introduction

A very common failure mode for coated tools and wear parts for machinery is delamination in response to the external forces acting on the surface. This may be a catastrofic way of failure for the application, whereas a more acceptable failure mode is gradual and continuous wear throughout the lifetime of the coated part. Thus there is a need to assure strong adhesion of the coating to the surface of the part to be coated. A prerequisite for this is that the surface is sufficiently free from impurities and adsorbed gasses before the start of the deposition process. Plasma cleaning of the surface is widely used prior to the deposition of thin films when the deposition temperatures are low, such as in PE-CVD of a-C:H. The method of plasma cleaning described here, has previously been used to obtain good adhesion of a-C:H on steel substrates [1].

Experimental

The vacuum chamber, regularly used for the deposition of a-C:H, was pumped by an oil diffusion pump capable of reaching a base pressure of less than $4 \cdot 10^{-5}$ Pa. An RF power supply (13.56 MHz) was connected through a coaxial cable to the electrode, which was resting on a grounded metal plate, the two separated by a 2mm thick insulating alumina plate. In this configuration the discharge was highly asymmetric and a large selfbias was easily obtained on the electrode. Plasma cleaning was done on two types of electrode material, a stainless steel AISI 316 and an aluminium alloy, AlMgSi1 (DIN). The diameter of the electrodes was 80 mm. The discharge parameters throughout the experiments were 6.0 Pa gas pressure and 20 sccm argon flow. A selfbias, V_{bias}, of -300 volt was used resulting in an approximate current density of 2 mA/cm^2 on the electrode.

The light emitted perpendicular to the electrode surface was monitored. Only a part of the surface was viewed by the optical system. The wavelength resolution was 1.1 Å. All spectra were obtained using 30 seconds integration time. The system has been described in detail elsewhere [2]. Langmuir probe measurements were done using a commercially available system with an RF compensated probe equipped with a 10 mm long tungsten probe tip with a diameter of 0.15 mm. This particular probe design has been described by Chatterton et al [3]. The probe was mounted parallel with the electrode surface and placed above its center 30 mm into the glow region. OES spectra and probe IV-curves could be obtained simultaneously.

Methods of evaluation

The removal of water vapour was monitored indirectly by looking at the emission present in the discharge from the OH and H radicals, resulting from the dissociation of water. In this study we monitor the entire complex around 306.4 nm of OH, the 656.3 nm H_α line and the 486.2 nm H_β line. A number of argon lines were also recorded for the purpose of intensity reference. By taking the ratio between a radical line and a constant argon line we may compare directly different cleaning runs. Mainly the argon 573.95 nm line was used for this purpose.

The plasma parameters were evaluated as done by Cox [4]. The electron temperature was found from the slope of the IV-curve in the retardation region as $kT_e/e = dV/d(\ln I_e)$. The floating potential V_f was taken to be the voltage where the probe current was zero. The plasma potential V_p was obtained as the voltage where the linear fit to the electron current in the retardation region intersected with the linear fit to the electron current in the saturation region. The relative uncertainty of the electron temperature is estimated to about 5%, but absolute uncertainties will surely be higher.

Results and Discussion

The base pressure obtained prior to the plasma cleaning was important. If the

discharge was started before a good base pressure had been reached, very high levels of H emission was seen. The curves in Fig. 1 were obtained with a poor base pressure of $1 \cdot 10^{-3}$ Pa. For the aluminium electrode it is clearly seen that the electron temperature increases over time. Less so for the steel electrode. Note that the emission ratio of H_α to the Ar 573.95 nm line is lower for the steel electrode. The curves in Fig. 2 were obtained with a base pressure prior to cleaning of less than $4 \cdot 10^{-5}$ Pa. Comparing the intensity level of H_α from the steel (▽) electrode in Fig. 2 to that shown in Fig. 1 there is a difference in the H_α level of a factor 6. Unfortunately the emission ratio for the aluminium electrode shown in Fig. 2 cannot be compared as it was obtained using H_β and the Ar^+ 463.72 nm line. With the smaller concentration of H in the discharge the measured electron temperatures were practically constant around 2.1 eV for both the aluminium and the steel electrode.

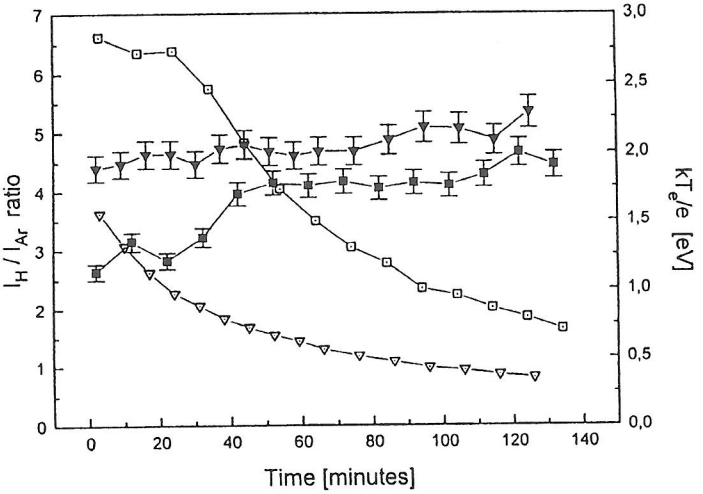

Fig. 1. Electron temperature (closed symbols) and intensity ratio (open symbols) of H_α to Ar 573.95 nm, shown for two different electrode materials, AlMgSi1 (■,□) and AISI 316 (▼,▽), as a function of cleaning time. The base pressure prior to cleaning was $1 \cdot 10^{-3}$ Pa.

To investigate the role of hydrogen (without influence from any oxygen) we deliberately added H_2 to the argon gas flow. On previously cleaned electrodes the amount of emission from H_α was recorded together with the electron temperature. The results can be seen in Fig. 3. Again we see a large difference in the emission ratio, with very little emission when using the steel electrode. For the aluminium electrode the H_α emission is approximately linear with the amount of added H_2. While the electron temperature drops when the electrode material is aluminium, it remains constant when using the steel electrode. The reason for this must be that the steel electrode favors recombination of atomic hydrogen into molecular hydrogen H_2.

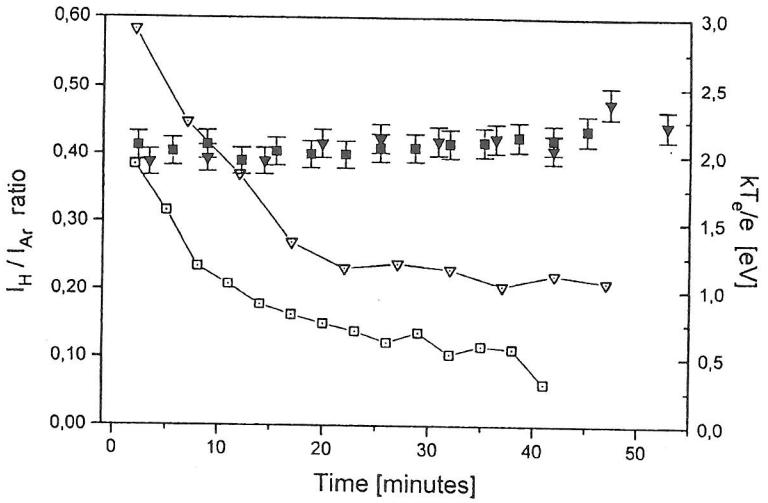

Fig. 2. Electron temperature and intensity ratio of H_β to Ar^+ 463.72 nm using AlMgSi1 (■,□) electrode, and electron temperature and intensity ratio of H_α to Ar 573.95nm using AISI 316 (▼,▽) electrode, both shown as a function of the cleaning time. The basepressure prior to cleaning was less than $4 \cdot 10^{-5}$ Pa.

When no H_2 was added, the electron temperatures as well as the emission intensities approached each other at 2.1 eV. Even so, we generally found V_p and V_f for the steel electrode to be about 6 volt higher than for the aluminium electrode. Possible explanations could be a difference in RF conductivity or a difference in the secondary electron emission of the electrodes.

Electron densities where found to be on the order of $2.5 \cdot 10^{10}$ cm^{-3} whereas the ion densities were around $4 \cdot 10^{10}$ cm^{-3} when evaluated as done by Cox [4].

In Fig. 4 we show the corresponding emission ratio of the OH 306.4 nm complex to the Ar 573.95 nm line and the similar ratio for emission from them Al 396.15 nm line. The curves have been normalised to the initial intensity. Open symbols indicate that the base pressure prior to cleaning was less than $4 \cdot 10^{-5}$ Pa, closed symbols $1 \cdot 10^{-3}$ Pa. In both cases aluminium was sputtered at an increasing rate as the cleaning progressed. As expected the OH signal was seen to drop during cleaning. Assuming exponential decay a time constant was found for both cases of base pressure by fitting to the OH curves (broken lines). For the low base pressure of $4 \cdot 10^{-5}$ Pa the time constant was 10.5 minutes, and for the high base pressure of $1 \cdot 10^{-3}$ Pa it was 103 minutes. The interpretation of this difference is that the amount of desorption of H_2O from the chamber determines the amount of OH emission seen in the discharge. The rate of desorption is given by the temperature and the pressure. Until desorption/adsorption from the chamber walls is in equilibrium with the chamber temperature at a given pressure, the time constant reflects the desorption rate from the chamber walls (in our case for $1 \cdot 10^{-3}$ Pa). If such an equilibrium exists when the plasma cleaning is started

(in this case for $4 \cdot 10^{-5}$ Pa) desorption is mainly from the electrode, and as it is heated by the ion bombardment (including the effect of the sputtering) a shorter time constant is obtained. The same behaviour was observed with the steel electrode.

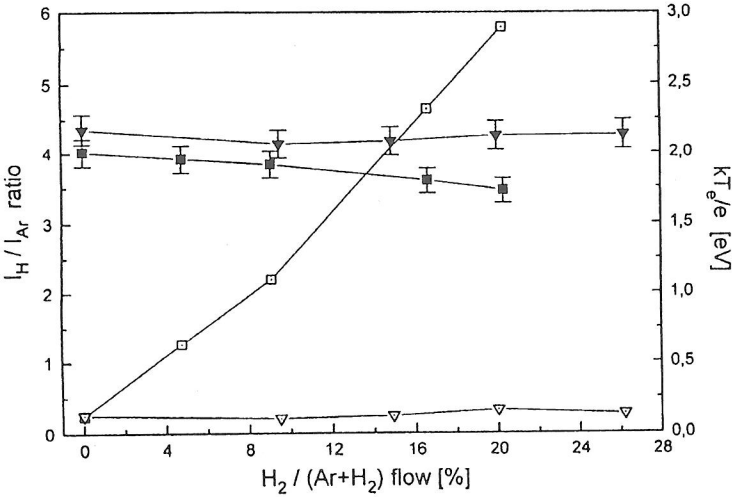

Fig. 3. Electron temperature (closed symbols) and intensity ratio (open symbols) of H_α to Ar 573.95 nm shown for two different electrode materials, AlMgSi1 (■,□) and AISI 316 (▼,▽), as a function of H_2 addition to an argon cleaning plasma.

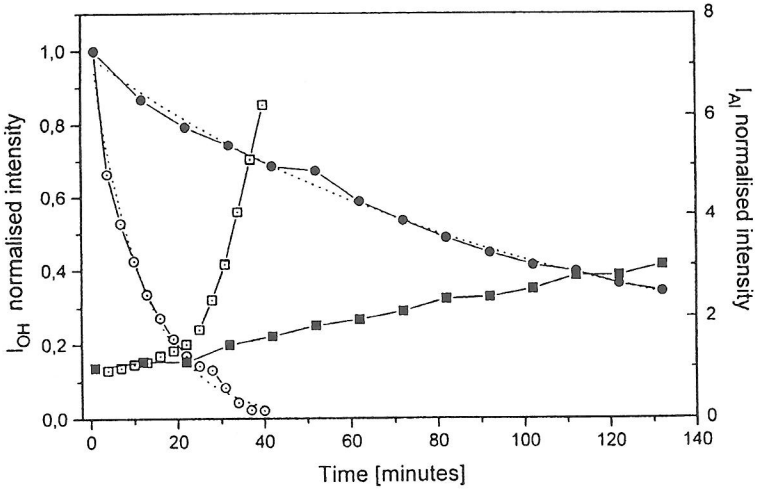

Fig. 4. Emission ratio of OH 306.4 nm (o ,•) and Al 396.15nm (□,■) to Ar 383.45 nm shown for two values of basepressure, $4 \cdot 10^{-5}$ Pa (open symbols) and $1 \cdot 10^{-3}$ Pa (closed symbols), as a function of cleaning time. The ratio was normalised to the start of the cleaning.

Summary

We have investigated the removal of water vapour by monitoring the emission of light from the OH and H radicals which are products of the dissociation of water during plasma cleaning. Two time constants were associated with the removal of water, one corresponding to a situation where desorption from the chamber walls dominated, and one in which desorption was principally from the electrode. The time constants were found to be 10,5 and 103 minutes respectively.

The removal of water was associated with a large increase in the optical signal of sputtered electrode material for both AISI 316 and AlMgSi1.

A slight increase of the electron temperature to a final value around 2.1 eV is probably due to the removal of hydrogen. With additions of H_2, a significant difference was observed in the H_α emission from cleaning plasmas in the case of an aluminium versus a steel electrode. With the aluminium electrode the H emission signal increased linearly with the amount of H_2 added. For the steel electrode the H_α emission level staid constantly at a low intensity.

Both materials exhibited an increase in their sputter rate as a function of cleaning time.

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