Application of atmospheric pressure dielectric barrier discharges in deposition, cleaning and activation

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Abstract

Dielectric barrier discharges (DBDs) at atmospheric pressure are obtained using mixtures of He and Ar as carrier gasses and various reactive additives such as hydrocarbons, hydrogen and nitrogen. These DBDs are used in three applications: deposition of polymer films; cleaning of Ag and Cu substrates; and activation of polyurethane and steel surfaces. In the case of the film deposition, several process conditions are investigated and the resulting films are analysed by scanning electron microscope, Fourier transform infrared spectroscopy and NMR. In another series of experiments Ag and Cu surfaces, covered with sulfide and oxide layers, are treated by means of a DBD in helium or argon with hydrogen added. The surfaces are analysed with X-ray photoelectron spectroscopy. Finally, a He–N\textsubscript{2} plasma is used as an activator of polyurethane. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the early 1990s the low temperature atmospheric pressure glow (APG) plasma technology was developed [1–4]. Although the characteristics of these discharges are in many aspects different from their low-pressure counterparts, it has become clear that their chemical and physical properties make them interesting tools in materials technology. In addition to the industrial commercialised ozone generation a lot of new applications are under investigation. The cleaning and activation of surfaces as well as the deposition of polymer-like coatings have been demonstrated conclusively and draw increasing industrial attention [5].

The configuration that is commonly used for the stabilisation of diffuse glow discharges at atmospheric pressure is the (so-called) dielectric barrier discharge. At least one of the electrodes is covered with a dielectric material and an AC-field in the range from 50 Hz to 500 kHz is applied to the electrodes. In this case a transient, spatially uniform glow can be observed. The most important characteristic of these DBDs is that the non-equilibrium plasma conditions can be achieved at atmospheric pressure. A discussion of this phenomenon can be found elsewhere [6–8].
This paper reports approximately three applications of DBDs:

1. polymerisation of ethylene;
2. cleaning of Ag and Cu surfaces; and
3. activation of polyurethane.

2. Experimental set-up

The experimental set-up (Fig. 1) consists of two disk-shaped Al electrodes with a diameter of 150 mm, both covered with an Al$_2$O$_3$ plate of 2 mm thickness. The gap between the un-cooled electrodes can be increased up to several centimetres. However, to ensure stable plasma operation the gap width is typically limited to a few millimetres.

To reduce air contamination the configuration is mounted in a vacuum chamber which is evacuated and subsequently filled with the process gas mixture. However, as technical-grade gases with standard purity are used, impurities are inevitably present. In fact, optical emission spectrometry revealed traces of N$_2$, CO, CO$_2$, and water in most plasmas (see Section 3). It should be borne in mind that these molecules can influence the plasma processing, in particular in those cases where certain elements have to be avoided in the process under consideration [7].

The flow rate is controlled by mass flow controllers and varies between 1 and 20 l/min depending on the process. The DBD is produced by means of a 20-kV/200-mA AC power source with variable frequency. Most experiments are run at frequencies between 1 and 4 kHz.

3. Dielectric barrier discharges in He and Ar at one atmosphere

As mentioned above, optical emission spectra are first recorded in the carrier gases, in order to assess the purity of the working gas.

Fig. 2 shows the optical emission spectra (OES) of a DBD in He and Ar, sampled through an optical fibre placed at a distance of a few centimetres from the discharge. The optical fibre is connected to the spectrometer, which has a focal length of 320 mm.

The emission spectrum in helium contains spectral bands of N$_2$ (second positive system), N$_2^+$ (first negative system), CO$^+$ (first negative system), CO$_2^+$ (Fox system) and OH (3064 Å system). Practically no helium lines are observed. From the mentioned set of spectral lines, only the N$_2$ and OH lines are present in argon. The argon spectrum shows additional lines, from NO (4th positive system) and from argon in the near infrared.

The presence of OH lines in both spectra reveals the presence of water as a contaminant [9].

A qualitative explanation for the other lines in the carrier gas spectra can be formulated based on the energy levels listed in Table 1. In argon, energy transfer from the 11.5-eV metastable energy level will dissociate molecular nitrogen, leading to NO formation. In helium, the Penning level energy is higher and sufficient to ionise N$_2$, CO$_2$ and CO, where the latter is produced by CO$_2$ dissociation. NO is not observed, probably because ionisation of nitrogen is more likely than dissociation. The absence of helium lines and the presence of the first negative system of N$_2^+$ in the helium spectrum suggests that the energy transfer is mainly by the Penning mechanism [10].

4. Dielectric barrier discharges in mixtures of He and Ar with ethylene

Polymerisation of hydrocarbons in a DBD at atmospheric pressure is a spontaneous and fast process [11,12] and as such very promising for future industrial
processes for growing polymer-like materials for protection, lubrication, etc.

From the former discussion one could expect that the carrier gas (He and Ar) also influences the polymerisation process and that it is useful to establish a correlation between the carrier gas and the details of the polymerisation process. However, as will be shown in the example of the polymerisation of ethylene, simple spectral analysis cannot explain the observed differences and the polymerisation mechanisms remain highly speculative.

Polyethylene is made from a plasma of He or Ar mixed with ethylene in the proportion of 10–0.51/min. The substrates, silicon, glass and stainless steel, are placed on the lower (high voltage) electrode during 5–10 min. The Figs. 3 and 4 show the SEM cross-sections of the resulting deposition on silicon.

Some qualitative observations are readily made. Eth-

Fig. 2. Optical photon emission spectroscopy of a helium and argon dielectric barrier discharge at 1 atm pressure. The intensities are expressed in arbitrary units in which the most intense line is set to 100.
Table 1
Ionisation energies, metastable energy levels and bond strengths of the most recurrent molecules in He and Ar plasma's at atmospheric pressure

<table>
<thead>
<tr>
<th></th>
<th>Ionisation energy (eV)</th>
<th>Bond strength X–Y (eV)</th>
<th>Metastable energy level (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>24.6</td>
<td></td>
<td>19.8</td>
</tr>
<tr>
<td>Ar</td>
<td>15.8</td>
<td></td>
<td>11.5</td>
</tr>
<tr>
<td>N₂</td>
<td>15.6</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>13.8</td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. SEM cross-section of a deposition on silicon from a helium–ethylene plasma at atmospheric pressure deposition time 10 min.

ethylene polymerised in He gives a low density, sticky and opaque polymer. The Ar plasma on the other hand gives a clear and more solid polymer with good adhesion to all substrates. The polymer from the He plasma dissolves quite well in chloroform in contrast to the one obtained from the Ar plasma, which hardly get into solution. These observations indicate a difference in ‘polymer’ structure.

The infrared spectra of the polymers on stainless steel and silicon show no substantial difference. In both cases the characteristics of a polyethylene-like substance are present (Fig. 5). The C=O peak at 1696 cm$^{-1}$ indicates the presence of bonded oxygen in the
polymer, most probably originating from molecular oxygen when exposed to air [13].

On the other hand, the optical emission spectra of the two discharges are quite different from the pure plasmas (Fig. 6). In He, the ionised N$_2$ and CO lines have disappeared and He lines become more prominent. The CH line at 3889 cm$^{-1}$ [14] gives the only indication of the presence of ethylene in the plasma. The spectrum of the argon–ethylene plasma is almost completely quenched. There is a C$_2$ line at 5165 cm$^{-1}$ and the CH line at 4314 cm$^{-1}$, which is commonly observed in low-pressure plasmas too. There is also a relative shift in intensities of the Ar lines.

Preliminary NMR analysis of the polymer from the He plasma allows more qualitative conclusions. Proton spin relaxation measurements indicate impurities (including O), the existence of the C=C double bond and a polyethylene disproportionate large CH$_3$ contribution (as present at the end of polymer chains). Moreover, complementary $^{13}$C measurements only show a diffuse and broadened peak indicating very fast relaxation, commonly attributed to strong paramagnetic sites.

All these results suggest that (in case of the helium/ethylene plasma) there is not a polymerisation in the strict sense of the word. There is merely a partial breaking down of the monomer and a radicalisation by interaction with the activated He or Ar gas. The coating or deposition, then, is formed by sticking of these radicalised fragments to the surface of the electrodes (or a substrate) forming a rather low density, random cross-linked network with a considerable amount of radicals, to which oxygen becomes bonded when exposed to air.
For the argon/ethylene polymer, NMR measurements are not available to date yet.

5. Treatment of Ag and Cu surfaces

Another application of DBD is the treatment of surfaces for several purposes. The applicability of DBD for cleaning of metal surfaces like Ag and Cu is demonstrated here. The dark silver sulfide layer, which forms on silver as a result of ageing, and the oxide layer on copper are removed successfully by means of a plasma of Ar or He containing 5% H₂. The impact of the plasma is studied by X-ray photoelectron spectroscopy.

After a treatment of 3 min in the DBD set-up described above, the sulfide layer on Ag substrates under investigation is totally removed. The successive applications of a helium/hydrogen plasma results in a gradual decrease of the Ag₂S layer as can be concluded from XPS measurements (Fig. 7) but is also confirmed simply on visual inspection.

The observed effect is of chemical nature what can be concluded from the indisputable presence of H₂S in the exhaust of the reactor. Most probably, it is a radical process initiated by the radicalisation of the hydrogen atoms that subsequently bind to the sulfur forming H₂S. Unfortunately, optical emission spectra of the hydrogen containing plasmas could not reveal the presence of H conclusively.

Although the effect is less spectacular, also chloride layers can be removed from a Ag surface submersed in a hydrogen plasma (Fig. 7).

Similar metallic reduction by hydrogen plasmas can also be observed in the oxide layer of a less precious metal like Cu (Fig. 7). Under the action of the hydrogen plasma the surface layer, basically CuO before treatment, becomes oxygen poor close to the surface indicating metallic copper, slowly turning into a compound which is more like Cu₂O, until finally at larger depth, the CuO stoichiometry is reached again.

6. Activation of polyurethane

As a third example of the use of the atmospheric pressure DBD the surface treatment of polymers, in particular polyurethane slabs in order to achieve a better adhesion to stainless steel plates [15], is investigated. A good adhesion of polyurethane to (stainless) steel by means of industrial adhesives needs proper preparation of both surfaces, commonly achieved by means of chemical pre-treatment. This process is complex and causes environmental problems. Moreover, a satisfying result is not always guaranteed.

Plasma treatment may not only be a fast and easy substitute for chemical treatment, but also the adhesive strength can be increased. In a series of test stainless steel samples as well as polyurethane samples are treated with helium DBD, pure or mixed with nitrogen and ethylene. Helium is chosen because argon appears to be not efficient enough as an activator. The explanation may be found in the presence of N²⁺ ion in He. Also the sticky characteristic of polymerised ethylene in case of He is in favour of this carrier gas.

Two types of commercial adhesives are used: Bostik 1400 and Scotch Weld 2216. Treatment of steel as well as polyurethane with a DBD of He or He/N₂ mixture (5%) does not give any considerable improvement in the overall adhesive contact strength, i.e. the adhesives commonly give way easily from the stainless steel. Finally, it turns out that a traditional chemical treatment of the steel substrate and a plasma treatment of the polyurethane by means of a He or a He/N₂ DBD [16], gives the best results. Fig. 8 shows the fracture energy of the adhesive contact between chemical pretreated stainless steel and plasma treated polyurethane.

As a result, one could expect that the treatment of both components, polyurethane and steel, with a He/N₂ and He/ethylene plasmas, respectively, should provide the strongest joint, at the same time making chemical pre-treatment redundant. Therefore, a more elaborate investigation is presently going on aiming for the replacement of chemical surface treatment by DBD processing.

7. Conclusions

The emission spectroscopy of a He and Ar DBD discharge at atmospheric pressure reveals high intensities of impurity bands. These impurities influence discharge stability and are also supposed to influence the
polymerisation process. Helium/ethylene and argon/ethylene plasmas give rise to two different types of coating. However, simple spectral analysis cannot explain the observed differences and the polymerisation mechanisms remain highly speculative. Furthermore, it is demonstrated that it is possible to remove oxide, chloride and sulfide layers from metal surfaces like Ag and Cu by means of DBD treatment. Finally DBDs are used as an activator of polyurethane surfaces. The adhesive/polyurethane bond after treatment is clearly stronger and a more elaborate investigation is presently going on.
Fig. 8. The fracture energy of the adhesive contact (for two commercial adhesives) between stainless steel and polyurethane as a function of pre-treatment of the polyurethane surface (effect of plasma treatment). The stainless steel was pre-treated with a traditional primer.

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References