SURFACE NANOTREATMENT OF SILICON AND POLYAMIDE BY MEANS OF ATMOSPHERIC MICROWAVE PLASMA JET

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1. ABSTRACT

The exposition to plasma can modify surface layer of various materials, typically with penetration depth around several nanometres. In this paper, the atmospheric pressure microwave argon plasma jet was used as the plasma source. Surface modification is caused, among others, by highly reactive species like O, N, OH, which are formed by mixing the plasma excited argon gas with surrounding air. We report on the results of the plasma treatment of silicon wafers and Polyamide 12 foils. We analysed selected parameters like surface energy and surface roughness of the samples by contact angle measurements and atomic force microscopy (AFM), respectively. We observed an increase in surface energy and therefore an enhanced wettability (water contact angle as low as 5 degrees) after the plasma treatment. This was accompanied by slight changes in roughness, too. We found that our plasma treatment process is quite fast, as significant changes of surface energy were observed for very short exposition times (tens of milliseconds). We performed also a study of the ageing of the treated samples. Optical emission spectroscopy (OES) was used as plasma diagnostics tool during the nanotreatment process, giving such results like the relative abundance of various species or the temperature of the plasma itself.

2. INTRODUCTION

Microwave (MW) discharges at atmospheric pressure, especially surface wave sustained discharges, have been investigated over the last decades both experimentally and theoretically [1]. Surface wave discharges can generally operate in a broad range of experimental conditions: pressures from 1 Pa to 10^5 Pa, frequencies from 200 kHz to 10 GHz [2], discharge dimensions from 10^{-3} m to 1 m and in various gases [3]. Flexible operating conditions provide a wide range of processing applications such as thin film deposition, gas decontamination, plasma sterilisation, light sources and lasers, particle production, materials processing etc. [4, 5, 6, 7].

Surface wave driven atmospheric discharges can be also used for plasma surface treatment which induces e.g. chemical changes, activation, cleaning, grafting, cross-linking, dangling bonds, wettability changes etc. These changes in surface properties can be induced by plasma generated species (electrons, ions, radicals, UV radiation etc.) [8]. Typical uses of microwave atmospheric jets are the localised or elevated temperature treatment, for rough and structured materials, and in surface modification accompanied by deposition. For this purposes it can be advantageous (economy, low electromagnetic interference, etc.) to use the microwave discharges over competing types as they have generally higher power density, which can positively influence both homogeneous and heterogeneous plasma-chemical reactions.

Silicon surface plays important role in current technologies, including micro-electronics and photovoltaics [9, 10]. The process of surface cleaning, smoothing, etching etc. includes almost always a rather complicated ``wet'' chemical process [10, 11, 12]. Recently, there is a tendency to replace these steps by plasma based technology which could provide an environmentally attractive alternative.

Polyamides are important engineering materials with wide range of applications in domestic and housing-related outlet [13]. Polyamide 12 (PA12) is a thermoplastic that is rigid, hard wearing and is resistant to oils, solvents and alkalis. A known problem with the polymers is their weak hydrophilic properties, which affects their wettability, printability, adhesion, etc. This can be solved by increasing the surface energy by a convenient method of surface modification [14, 15].

In this work we focused to find the conditions for which the surfatron plasma treatment would lead to sufficient hydrophilisation of the silicon and the polyamide. Other important parameters for plasma treatment are the exposure time and the ageing effect.

3. EXPERIMENTAL

We have used one particular type of atmospheric pressure microwave jet – the surfatron [16]. The surface wave discharge is produced by applying a high frequency electric field intensified by narrow slit to a gas flowing in a discharge tube. The microwave generator (frequency 2.45 GHz) is operated in sinusoidal amplitude modulated mode with the mean power of 250W and amplitude modulation frequency of 260 Hz. The wave launcher (surfatron) is fed via ferrite circulator and coaxial cable. The surfatron device is a modified SAIREM Surfatron 80 with integrated matching. Using this matching we maintained the reflected power below 10 W, which is the lowest limit of our power sensor. Thermal management is carried out (see Figure 1) by water cooling of the generator, circulator and surfatron itself.

Additionally, the fused silica discharge tube (1.5 mm and 4 mm inner and outer diameter, respectively) is cooled by compressed air. The end of the discharge tube is 2 cm from the launching gap. The flow of working gas, argon, is maintained at 1.45 slm (standard liter per minute) by a flow controller.

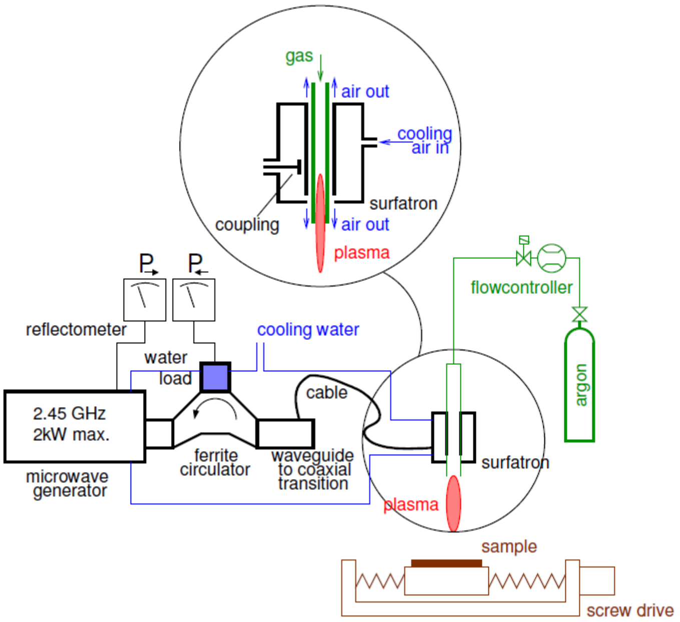


Fig.1 Schematic drawing of the experimental setup.

For diagnostics, the optical plasma emissions are collected by optic fibre, placed perpendicularly to the plasma axis and measuring the middle of the flame, and analysed by spectrometer FHR 1000 monochromator Jobin-Yvon Horiba (1.0 m focal length, Czerny-Turner type, grating 2400 gr/mm, CCD camera, specified resolution 8 pm). The surface roughness is analysed by AFM Auto Probe CP-Research from TM Microscopes, maximal vertical resolution 0.025 A. The Gwyddion [17] software was used to render images of surfaces.

We used silicon substrates (polished N-type, doped with antimony, Si (100) cut) having resistivity (5-18).10^{-3} Ω.cm purchased from ON Semiconductor. Before the plasma treatment experiments all samples were cleaned by isopropyl alcohol-cyclohexane mixture (1:1), dried by flow of air, then immersed in 1% HF solution at room temperature for 45 s for native oxide removal and finally dried by flow of air again.

Polyamide (PA 12) samples were cleaned by isopropyl alcohol-cyclohexane mixture (1:1) before the plasma treatment.

The silicon and polyamide samples are placed on motorised sample holder and conveyed into a direct contact with the plasma jet.

We determine surface free energy (SFE) of the samples by sessile drop technique, i.e. from the contact angle between the solid surface and the surface of a drop of liquid placed on it. The contact angles are measured directly from the images of the sessile drop (1.5 µl volume) taken with digital camera of Surface Energy Evaluation System [18]. Surface free energy of silicon samples are calculated using Owens-Wendt two liquids model [19].

4. RESULTS

The plasma has elongated form, starting in the discharge tube and ending in diffuse flame outside the discharge tube. The optical emission spectrum is recorded in the range of 250 – 750 nm. The result is shown in Figure 2. Despite the discharge being ignited in a pure argon, the spectrum is dominated by OH system ($A^2\Sigma^+ \rightarrow X^2\Pi$) and consists of argon lines, 2nd positive system of nitrogen ($C^3\Pi_u \rightarrow B^3\Pi_g$), and molecular bands of NO. These impurities come from the surrounding air as it is mixing with the plasma flame. The OES cannot fully determine the composition of the plasma as some species can be in the ground state or their emission lines (or bands) are outside the observed wavelength range. E.g. the ozone, despite being produced by the jet, is not observed in our emission spectra.

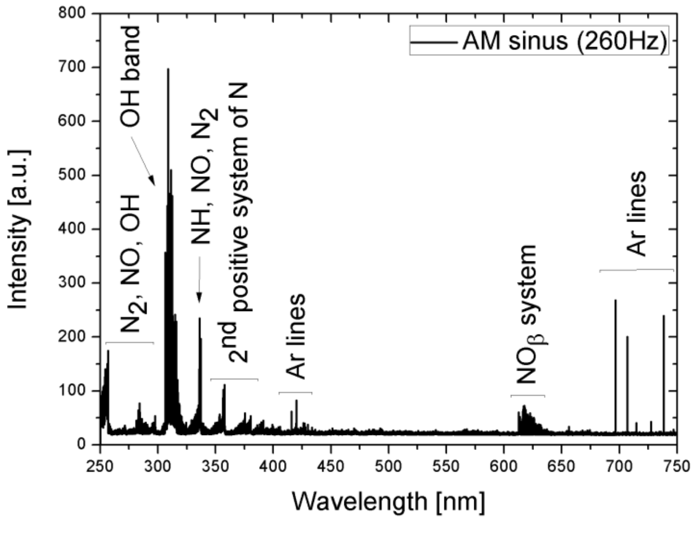


Fig.2 Overview of the emission spectrum in the surfatron atmospheric plasma jet at input mean power 250 W and in 1,45 slm of argon.

The left graph in Figure 3 shows the dependence of water contact angle on exposure time, the right graph shows the corresponding values of the surface free energy calculated by Owens-Wendt two liquids model. It is evident, that prolonging the exposure from 0,019 s up has no increased effect, as the water contact angle (5±1)° and SFE (72±1) mJ/m^2 stay constant.

The plasma surface modification is not entirely permanent as OH groups slowly disappear from the surface. The ageing effect is one of the significant parameters for the evaluation of the quality of plasma treatment.

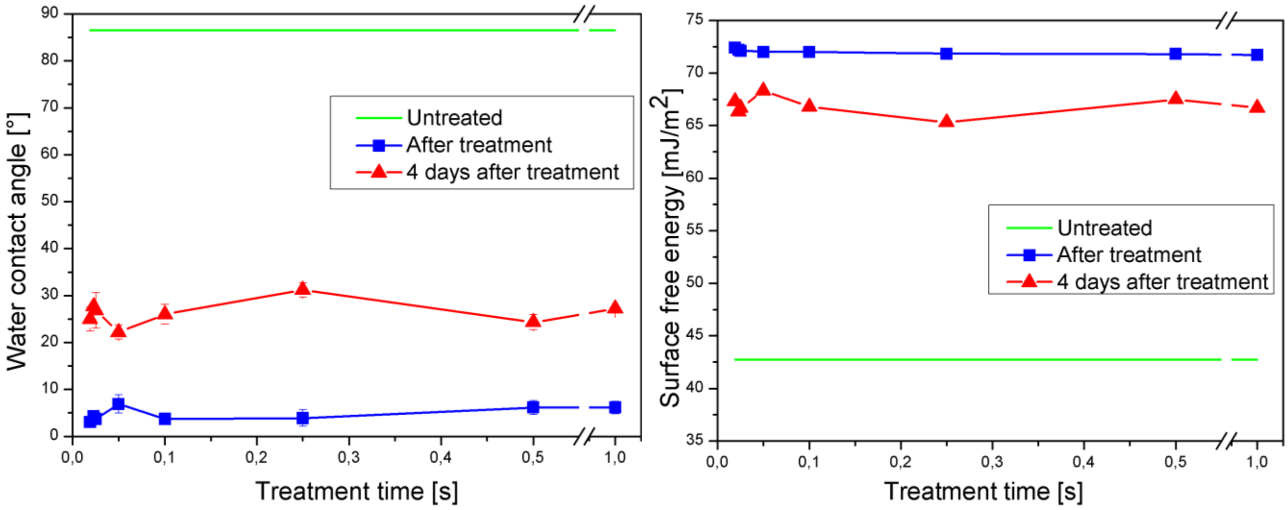


Fig.3 Plasma treatment on silicon wafers for different exposure times (1,45 slm Ar, mean power 250W, AM sinus, 260Hz). On the left graph there is water contact angle of untreated, treated and of 4 days old treated samples. On the opposite side there is a surface free energy for the same conditions calculated by Owens-Wendt two liquid model.

Another set of samples were treated with plasma for different exposure times and then left untouched for four days in air (23°C, humidity between 20% and 40%). After that, the samples were measured to determine the ageing. The results (Figure 3, red triangles) reveal an increase in the water contact angle (26±2)° due to the aging but even after four days the samples did not show any influence of different treatment durations.

Figure 4 shows treated and untreated parts on silicon and polyamide samples. Left picture in Figure 4 even reveals approximate diameter of treatment spot on silicon (10 mm). The spot is considerably larger than inner diameter of the discharge tube (1.5 mm).

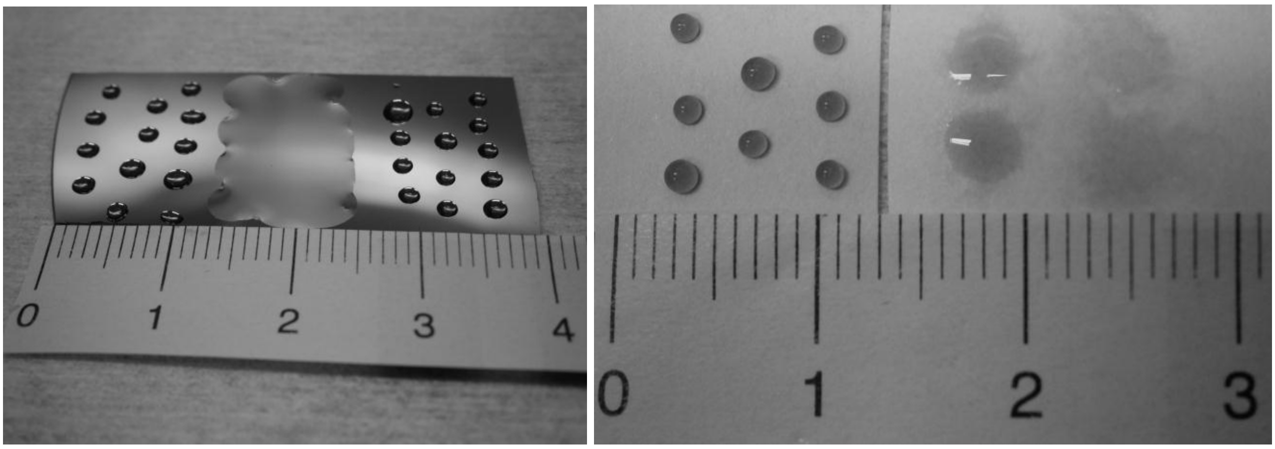
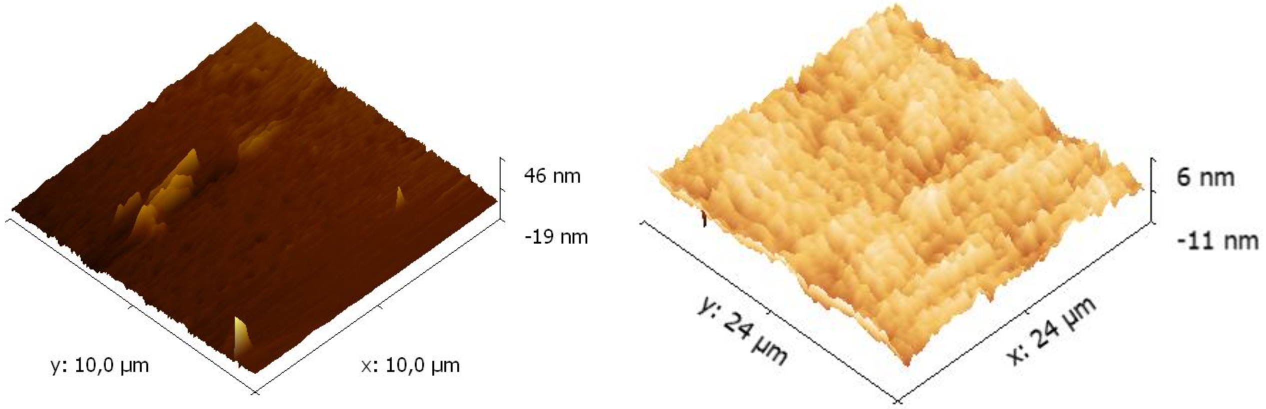


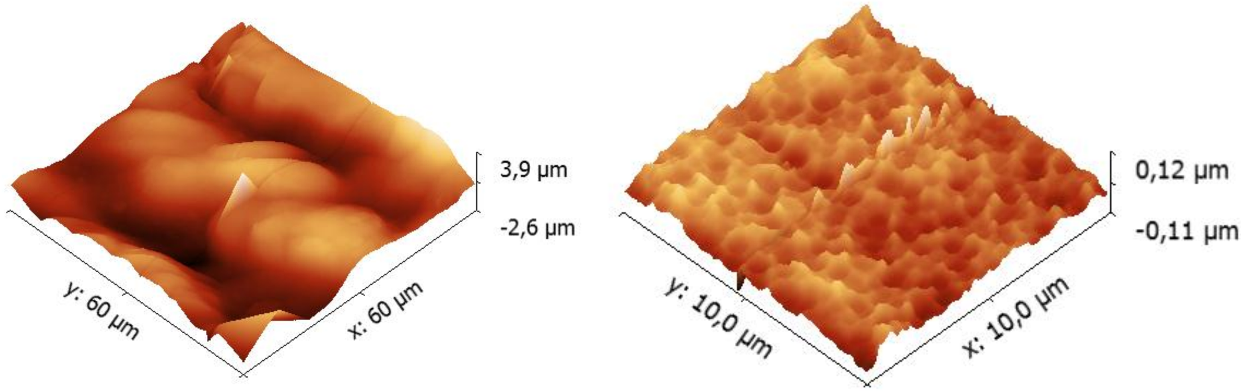
Fig.4 Plasma treatment of silicon wafer (on the left) and polyamide (on the right).

Figure 5 and Figure 6 represent AFM images of sample morphology (before and after plasma treatment) on silicon and polyamide. Silicon surface is not ideally cleaned (Figure 5a) but most of the surface shows no roughness. After 1 s of plasma treatment the silicon surface is measurably roughened (Figure 5b).



a) b)

Fig.5 Comparison of surface morphology of the silicon before plasma treatment (a) and after 1s plasma treatment (b).



a) b)

Fig.6 Comparison of surface morphology of the polyamide before plasma treatment (a) and after 1 s plasma treatment (b).

5. CONCLUSION

The atmospheric pressure surface wave driven argon plasma was successfully used for a plasma surface treatment of silicon and polyamide. Significant increase in wettability was observed for both materials. In the case of silicon samples, we found that surfatron plasma induces the chemical changes very fast - in a time interval shorter than 19 ms.

AFM measurements have shown that surface morphology of both materials is influenced by exposition to the plasma jet.

The experimental results show that despite relatively high temperature of the jet [20], it can be successfully used even for the treatment of temperature sensitive polymers like polyamide thanks to a high speed of the treatment.

ACKNOWLEDGEMENTS

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