GAS CHEMISTRY RELATED TO THE OPERATION OF MICROHOLLOW CATHODE DISCHARGES

VALENTIN FELIX[1], JUDITH GOLDA[3], PHILIPPE LEFAUCHEUX[1], LAWRENCE J. OVERZET[2], VOLKER SCHULZ-VON DER GATHEN[3], OLIVIER AUBRY[1], REMI DUSSART[1]*

[1] *GREMI, Université d'Orléans, Orléans, 45067, France*
[2] *PSAL, University of Texas at Dallas, Richardson, TX 75080-3021, USA*
[3] *Experimental Physics II, Ruhr-Universität Bochum, 44780 Bochum, Germany*
*remi.dussart@univ-orleans.fr

ABSTRACT

Instabilities obtained in silicon micro hollow cathode discharges (MHCD) were investigated using a high speed video camera and analysing SEM pictures of the electrodes after the operation of the microplasma. We show that the damage done to the electrodes of the microdischarge device is linked to the optical and electrical characteristics of the discharges. Modifications induced by these discharges in a gas mixture containing SF_6 were also studied using *in-situ* infra-red (FTIR) spectroscopy. This research is intended to help overcome the present limitations of such devices in order to make them more reliable and more robust.

1. INTRODUCTION

Microdischarges are spatially confined plasmas having at least one of their dimensions smaller than one millimeter. Over the two last decades, Microdischarges have attracted interest since they allow the possibility of making atmospheric pressure non-thermal plasmas.

When operating in a DC regime, these high pressure plasma sources show large electron density and intense optical emission [1]. They are of interest for chemistry based applications like gas abatement.

Silicon based devices were introduced and studied by several teams [2, 3]. They are produced in a clean room facility using classical semiconductor processes (deposition, lithography, etching, etc.). They are of interest for microsystem devices such as lab-on-chip, microsensors, etc.

However, the DC operation of silicon based devices does not produce a quiescent plasma : instabilities in the form of short and intense current pulses develop, leading to the rapid self-destruction of the devices. The formation mechanisms of these instabilities is reported in [2]. Current peaks as high as hundreds of milliamps are produced with a duration of a few hundreds of nanoseconds.

The formation of the instabilities in our silicon devices was studied in helium microplasma by electrical characterization and by a high speed video camera. Electrical measurements and optical analysis were synchronized in order to show the link between the electrical signal and the obtained images. In this paper, a mechanism for the microdevice failure is proposed based on the results of this characterization and on scanning electron microcosope (SEM) images of the cathode surface after operation.

A small amount of SF_6 was added to the helium microplasma in order to investigate its effect on the discharge. *In-situ* FTIR spectroscopy was carried out to monitor the chemical changes occuring in the microplasma. The results of FTIR experiments are also presented in this paper.

2. EXPERIMENTAL SETUP

For this study, microplasmas were made using sandwich type ($Si/SiO_2/Ni$) MHCDs operated with the silicon acting as the cathode. The fabrication process flow of these devices is detailed in

[2]. The silicon cavities had diameters of 100 μm or 150 μm and were either slightly isotropically etched or not etched at all. These samples are designed so that there are four electrodes on each chip (as shown in fig.1). Using this arrangement, four experiments could be performed on four identical devices without having to vent the chamber.

The chamber was designed to fit inside a FTIR spectrometer (Thermo Nicolet Nexus 470) that has a maximal spectral resolution of 0.125 cm^{-1}. It was also equipped with two ZnSe windows allowing a spectral range of 4000 cm^{-1} to 650 cm^{-1}. The sample was placed inside the chamber on a sample holder so that the infra-red beam was parallel to the sample surface at a distance of 1 mm.

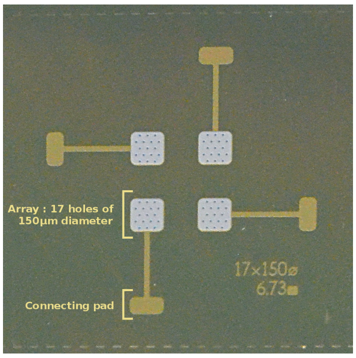

Fig. 1: Photograph of one electrode design, which consists of a 2 × 2 mm array of 17 cavities with a diameter of 150 μm. The connecting pad is placed 4 mm from the array to avoid arcing with the connector.

It should be noted that the sample holder is thermally insulated and cannot act as a heat sink for the sample. This means that we have no control on the sample temperature during the experiments.

Before each experiment, the chamber was evacuated to a base pressure in the 10^{-7} mBar range, then filled a first time with the working gas, pumped back down to 10^{-6} mBar and then filled back with the gas to the working pressure. In this study, we used helium and SF_6. The working pressure can be set between 100 mBar to 1200 mBar. Once filled, the chamber is sealed.

The MHCDs were powered through a ballast resistor by a DC power supply (Heinzinger PNC 1500-100). This power supply can be manually or remotely controlled by a function generator.

The electrical characteristics (voltage) were recorded using an oscilloscope (Tektronix TDS 3014B, 100 MHz) and data was stored on a computer. The current was deduced from the voltage drop across the ballast resistor.

A high-speed video camera (Keyence WV-600C) allowed us to monitor the dynamics of the emission of the plasma with a temporal resolution of 150,000 frames per second (fps). A higher sampling rate is possible but the exposure time becomes too small to detect the light emitted from the plasma above the noise level.

Finally, after operation of the microplasma, SEM observation of the electrodes was carried out to evaluate the damages caused by the plasma.

3. RESULTS AND DISCUSSION

The instabilities were characterized using the high-speed video camera. A picture of the microplasma is shown in fig.2. A single 150 μm diameter cavity was lit in 400 mBar helium with a current of 1 mA. The silicon was corresponding to the cathode side of the discharge. As observed in fig.2, a white and bright spot of 2-3 μm in diameter appeared from time to time during the operation of the MHCD. It originates from a random point over the cathode.

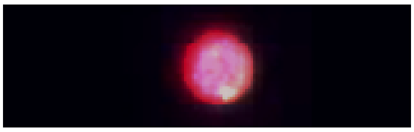

Fig. 2: *Image of a discharge in a 150 µm diameter cavity operated in 400 mBar of helium. The white dot at the bottom is due to the emission of an instability.*

Thus, a way to track these instabilities on the video is to look for the brightest pixels in each image. We have only observed a single bright spot at any given time. We have never found more than one developing at the same time. Electrical measurements showed that the duration of such events are of the order of a few hundreds of nanoseconds.

A comparison between the optical signal recorded by the camera and the electrical measurement recorded by the oscilloscope is shown in fig.3. The anode potential is plotted versus time in the lower part of fig.3. In the upper part of the graph the brightest pixel intensity is plotted. A quite high density of peaks was observed during this experiment. For each voltage drop on the anode (cathode was grounded), a bright spot appears that lasts for just one frame. This confirms the assumption that these bright spots are indeed linked to current instabilities.

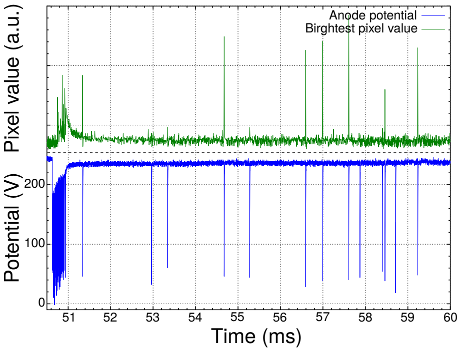

Fig. 3: Simultaneously recorded anode potential and value of the brightest pixels within the recorded images.

The value of the ballast resistor plays a significant role in the time constant of the "charging phase" of the device equivalent capacity (*i.e.* the delay between two instabilities) but has no effect on the instabilities themselves. Note that if the value of the ballast is too low, a too high electrical current will flow through the discharge, destroying the device immediately.

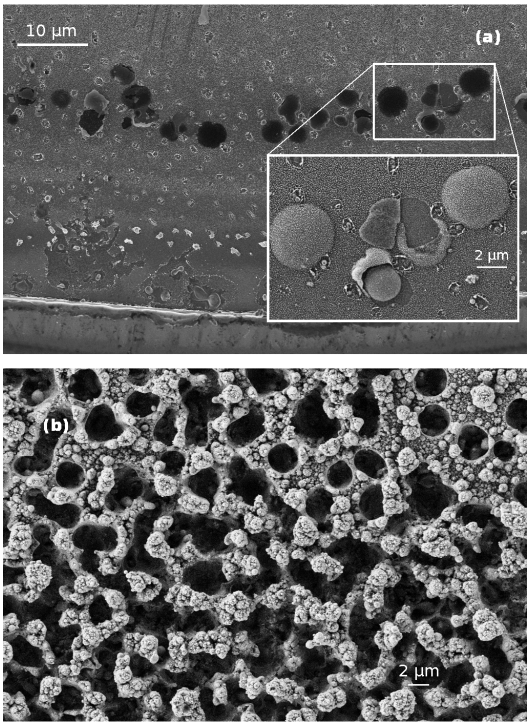

Fig. 4: SEM images of the traces left on the silicon by the instabilities of a helium microplasma (a) at 350 mBar and (b) at 700 mBar

The resulting typical damage caused by these instabilities on the silicon cathode is illustrated in fig.4 for the case of a helium discharge. This silicon surface was observed on a five cavity device after a 4 minutes plasma operation at 350 mBar with a current of 5 mA. A line of 2-4 μm diameter bubbles forms on the surface at a distance of the anode edge of about 27 μm. The bubbles are supposed to form due to the implantation of helium. This mechanism has already been reported at low pressure[4]. White spots were also observed during this plasma experiment at the edge of the cavities, at the same place where bubbles form. Consequently we can conclude that helium implantation is induced and favoured by the instabilities.

On the other hand, the morphology of the damage obtained with 700 mBar of helium is quite different (see fig.4 b). At this pressure only one microdischarge was ignited. The damage morphology is similar to those already reported [2, 5]. It is characterized by a high density of holes of 2 to 3 μm diameter. During the high current peaks, silicon material is ejected from the cathode, probably in liquid phase. Consequently, holes form at the place where silicon material is ejected. We checked that the electrical energy developed by each current peak is sufficient to melt the equivalent volume of a hole formed during this ejection mechanism. Silicon material from the ejections can also be found outside of the cavity on the nickel anode. The silicon deposition occurring on the dielectric can create a short circuit causing the failure of the device.

SF_6 was added to the helium in order to investigate its effect on the plasma. SF_6 is usually used to deeply etch silicon in low pressure plasma reactors : fluorine can react with silicon and create SiF_4 which is a volatile product.

To study the chemical reactions, a dedicated reactor was designed to fit inside a FTIR spectrometer in order to make *in-situ* measurements. In fig.5, we show the FTIR signal of the SF_6-He mixture before and after a 30 minute plasma.

A decrease of a factor of 4 in the SF_6 signal at 948 cm^{-1} was obtained which indicates that SF_6 gas was consumed during the plasma. A peak at 1030 cm^{-1} corresponding to SiF_4 is also observed after operation which shows that some silicon etching occurs in these experimental conditions. CO_2 and CO bands appear on the spectrum but they do not depend on the initial gas mixture and were observed even after a pure helium plasma. This is attributed to the always present carbon contamination of the samples.

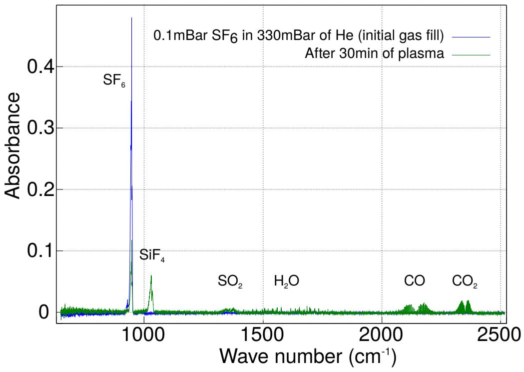

Fig. 5: FTIR spectrum of the gas composition before ignition and after 30 minutes of plasma operation.

During these experiments we noticed that the number of instabilities was significantly decreased. We also investigated the cavities by SEM after operation in such plasma composition. An example of a cavity profile is shown in fig.6. In this case, the surface is quite smooth compared to th surface after the pure helium discharge fig.4. The surface is smoothed by the silicon etching mechanism, but the cathode area increases with time which modifies the geometrical microdischarge characteristics.

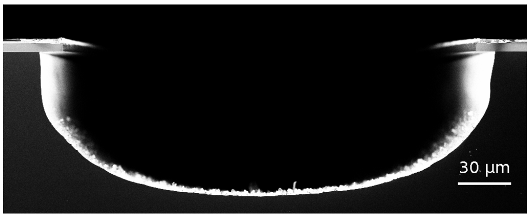

Fig. 6: SEM image of the cavity profile after operation in a He-SF_6 mixture plasma.

4. Conclusions

In this work, we studied the instabilities of microdischarges integrated on silicon, with the silicon acting as a cathode. We were able to link the current pulses to the aspect of the discharge and the damage on the electrode : high current pulses give bright and very localised optical emission spots. Depending on the pressure, they can lead to either the formation of bubbles due to helium implantation into silicon or to the formation of holes in the surface having diameter of a few micrometers. In this last case, silicon material is ejected from the developing holes onto other device surfaces and can cause the failure of the device.

In the presence of SF_6, some silicon etching was obtained as evidenced by FTIR spectroscopy and SEM observation. The rate of occurrence of the instabilities is significantly reduced by using this plasma mixture but the cavity geometry evolves with time.

Acknowledgments

JG and VSvdG are supported by PROCOPE grant 54366312 of the DAAD and Egide.
LJO was supported by the European Community 7th Research Program FP7/2007-2013 under grant agreement no 298741 and The University of Texas at Dallas.
VF, PL and RD aknowledge support in part by the French 'Agence Nationale de la Recherche' through contract no ANR-09-JCJC-0007-01 under the name SIMPAS project.
The microdischarge devices were made within the CTU IEF-MINERVE facility which is partly supported by the RENATECH network.

REFERENCES

[1] K.H.Becker, K.H.Schoenbach, J.G.Eden, Journal of Physics D: Applied Physics (2006), **39** R55-R70.
[2] M.K. Kulsreshath, L. Schwaederle, L.J. Overzet, P. Lefaucheux, J. Ladroue, T. Tillocher, O. Aubry, M. Woytasik, G. Schelcher, R. Dussart, J. Phys. D: Appl. Phys. (2012), **45** 065201.
[3] J.G. Eden, J.-S. Park, N.P. Ostrom, S.T. McCain, C.J. Wagner, B.A. Vojak, J. Chen, C. Liu, P. von Allmen, F. Zenhausern, D.J. Sadler, C. Jensen, D.L. Wilcox, J.J. Ewing, J. Phys. D: Appl. Phys. (2003), **36** 2869-2877.
[4] S. Igarashi, S. Muto, T. Tanabe, J. Aihara, K. Hojou, Surface and Coating Technology (2002), 421-425.
[5] R. Dussart, L.J. Overzet, T. Dufour, M. Kulsreshath, M.A. Mandra, T. Tillocher, O. Aubry, S. Dozias, P. Ranson, J.B. Lee, M. Goeckner, Eur. Phys. J. D. (2010).