Investigations in SF_6 and Cl_2/Ar plasmas used for titanium deep etching by means of mass spectrometry

T. Tillocher [(*)1], J. Golda [1], P. Lefaucheux [1] , B. Boutaud [2] , P. Ranson [1], R. Dussart [1]

[1] *GREMI, Université d'Orléans/CNRS, 14 rue d'Issoudun, BP 6744, 45067 Orléans cedex 2 France*
[2] *SORIN CRM, 4 avenue Réaumur, 92140 Clamart cedex, France*
[(*)] thomas.tillocher@univ-orleans.fr

Titanium can be deep etched to a few hundreds of µm with SF_6 and/or Cl_2/Ar plasma(s). A chlorine-based chemistry enhances the anisotropy of the profiles. However, reproducibility is low and a better understanding of the mechanisms would help to optimize etching processes. In this study, we present data of SF_6 and Cl_2/Ar plasmas chemistry under titanium etching conditions obained by mass spectrometry.

Titanium is a biocompatible material which is of great interest in the biomedical field for cardiology, surgery etc.... These last years, devices like bioMEMS have emerged with applications for biosensors, drug delivery and pacemakers. Their fabrication, where vertical sidewalls and smooth surfaces are required, is based on micromachining techniques derived from microelectronics technologies. Most of the research work reported in the literature relies on a Cl_2/Ar chemistry to deep etch titanium. Processes are performed at room temperature of the substrate with typical etch rates close to 1 µm/min and provide rather smooth surfaces [1, 2]. A patterned TiO_2 layer is often used as a hard mask. It has also been suggested recently that a thick (several 10s of microns) SU8 layer, a negative photoresist, can used as a mask for deep etching of titanium [3]. However, to our knowledge, the chemistry and the mechanisms involved in titanium deep etching are not yet completely understood.

The study we present here was performed in an Alcatel 601E ICP etching tool.The substrates were 4'' Ti wafers with various millimetric or submillimetric structures: circular and rectangular pillars and rings. We have investigated different mask materials: 40-45 µm thick SU8 layers, TiO_2 or Ni. This first investigation showed that Ni was the best candidate in our experimental conditions. Actuallty, the etched surface was rather smooth compared to what was obtained with the other mask materials. Mask sputtering and redeposition induced roughness with SU8 and the etch rate dropped dramatically with the TiO_2 mask. Wafers were cut into pieces and glued on a 6'' silicon carrier wafer. The carrier wafers were electrostatically clamped and the chuck temperature was regulated at 20°C. The process gases were SF_6, Cl_2, and Ar. Depending on the process run, helium flow could be used for thermal backside contact. Etched profiles were characterized using Scanning Electron Microscopy.

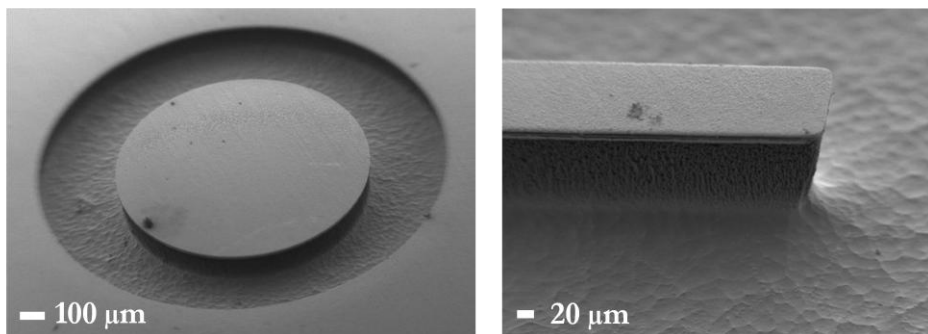

Fig. 1: Examples of features etched with a SF_6/Cl_2/Ar chemistry. Process time is 2h and etched depth is 127 µm. (20 mm x 20 mm sample glued on a 6'' Si carrier wafer)

Our results have shown that either a SF_6 plasma or a Cl_2/Ar plasma can be used to etch titanium. A SF_6 plasma helps to reach etch rates as high as 4 µm/min at higher pressures (a few Pa) but profiles are isotropic. A Cl_2/Ar chemistry at low pressure (almost 1 Pa) is preferred to get vertical sidewalls but, in this latter case, the etch rate is reduced. This is why we proposed to mix these two chemistries to

obtain the profiles displayed in figure 1. In this example, the mask was a 5 µm patterned Ni layer. The samples were etched for 2h and the substrate temperature was 20°C. The sidewalls are anisotropic and more especially negatively tapered. The depth is 127 µm, which represents an etch of almost 1 µm/min. The surface is fairly smooth. However, these performances are not reproducible since in most cases this process leads to a high roughness. Consequently, the etch rate is reduced.

This non-reproducibility may be due to the silicon carrier: $SiCl_x$ species, coming from the etch by-products of the silicon wafer may redeposit on the surface [5] and induce a micro-masking effect.

The plasma was characterized using a Hiden Analytical EQP mass spectrometer. This device can be used to analyse both neutral and charged species (positive and negative ions). In the first case, the species are ionized at their entrance in the system and discriminized as a function of the m/z number by the quadrupole mass filter. Ions can be analysed depending on their energy through an electrostatic sector and depending on their mass through the mass filter. The mass spectrometer was moved into the plasma bulk with a linear shift mechanism to analyse the plasma close to the samples.

The two chemistries (SF_6 and Cl_2/Ar) were studied separately as a function of time in different etching conditions: without any wafer, with a piece of titanium glued on the silicon carrier and a bare titanium carrier. Masses were scanned between 1 and 180 amu since no significant signal was detected for higher values. For neutral analysis, electron energy was set to 70 eV. Lower electron energy did not help to detect larger molecules or significantly increased intensities at larger m/z ratio. Typical spectra obtained for both chemistries are represented in figure 2. This helps to identify the species present in the plasma. We will present the study of their kinetics and propose preferential reaction pathways and physical mechanisms. Finally, we will correlate these results with the etching results.

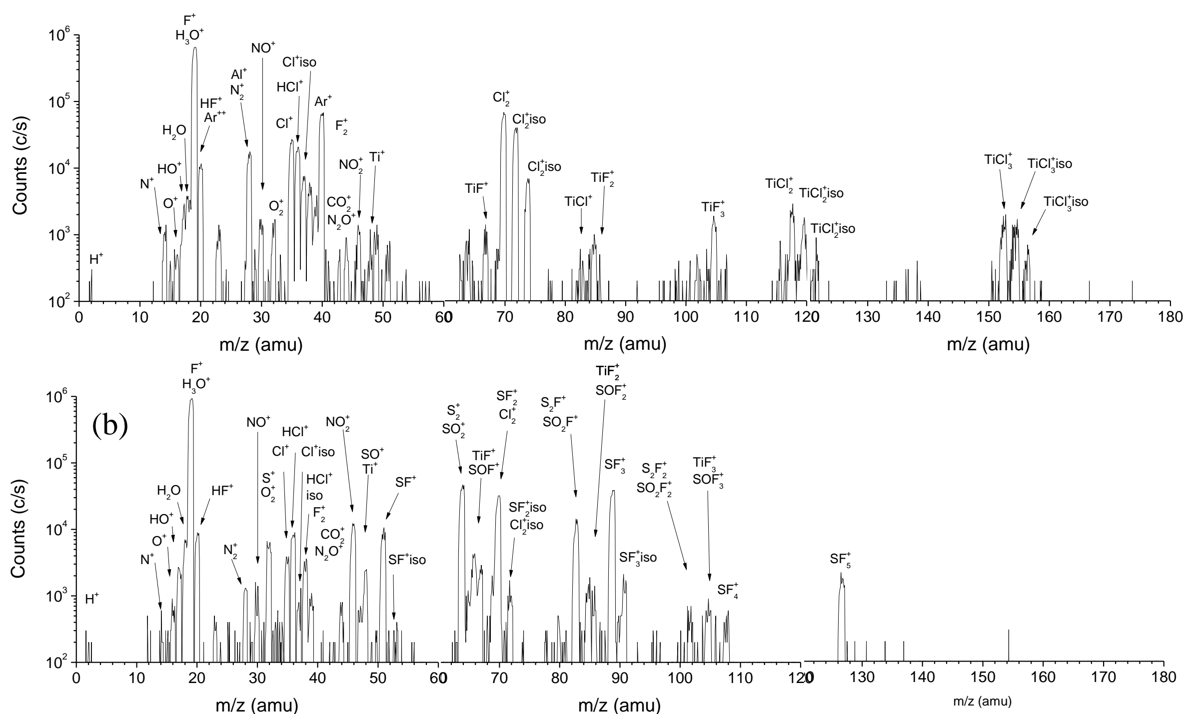

Fig. 2: Mass spectra of (a) a Cl_2/Ar plasma (1 Pa – 2000 W source power) and (b) a SF_6 plasma (1Pa – 1000 W source power) in presence of a titanium wafer.

References

[1] M.F. Aimi *et al.*, *Nature Materials*, **3** (2004)103.

[2] E. R. Parker *et al.*, *Journal of The Electrochemical Society*, **152** (2005) C675-C683.

[3] Gang Zhao *et al.*, *4th IEE Int. Conf. on Nano/micro Engineering and molecular systems*, 514 (2009)

[4] R. d'Agostino *et al.*, *Journal of Applied Physics*, **71** (1991) 462.

[5] C. Y. Dulard *et al.*, *Journal of Physics D*, **42** (2009) 115206