

## Nagendra Bhairamadgi

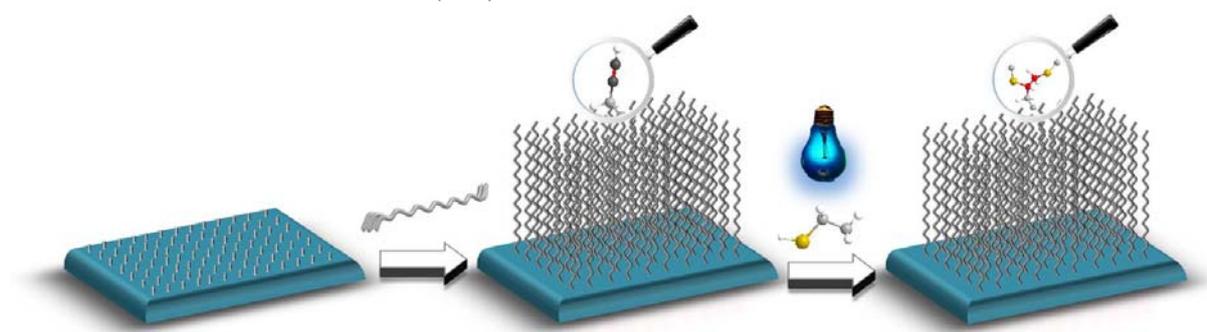
<b>Supervisor(s)</b>	Prof. Dr. Han Zuilhof and Prof. Dr. Cees van Rijn
<b>Project</b>	Surface functionalization via Thiol-Yne click chemistry.
<b>Fields of interest</b>	Surface chemistry, click chemistry, Polymer brushes, tribology
<b>E-mail</b>	nagendra.bhairamadgi@wur.nl
<b>Telephone</b>	+31 317 482364



### Introduction

Over the last few decades “Click Chemistry” has successfully attracted the attention of synthetic chemists, because these reactions are easy, require mild reaction conditions, are compatible with various solvents, tolerate different functional groups and products are obtained in quantitative yields with high purity. Click reactions have many applications such as synthesis of various (bio-)molecules, polymer grafting as well as in surface modification<sup>1-3</sup>.

Recently, we successfully modified Si(111) surfaces using thiol-ene click chemistry (TEC).<sup>4</sup> High surface coverage and stable surface towards oxidation were obtained after modification. However, it is seen that Thiol-Yne click chemistry (TYC) yields a higher surface coverage when compared with TEC, this is because of two reasons; firstly, because of the higher reactivity of TYC<sup>5</sup> and secondly, reaction of two thiol groups with one alkyne. There are additional advantages of using TYC over TEC namely, it is also observed that alkynes form densely packed and highly ordered monolayers on silicon surface when compared to alkenes<sup>6</sup>. Another advantage of alkyne-terminated monolayers is the ease for further functionalization of the monolayer using copper catalyzed alkyne-azide click reaction. Therefore, we aim to extend our previous findings of TEC to TYC on oxide-free Si(111) surface.



### Goal

Aim of this project is to obtain surfaces with improved physical properties such as low adhesion, low friction and wear resistant. To achieve this goal, we plan to develop a method to functionalize Si(111) surface using simple chemical reactions yielding high surface coverage.

## Progress

To determine the efficiency of click reactions on flat Si(111) surfaces, we compared the two chemistries namely TYC and TEC utilizing various functional groups such as thioglycolic acid, thioacetic acid, thioglycerol, thio- $\beta$ -D-glucose tetraacetate lactose and 9-fluorenylmethoxycarbonyl cysteine. Our initial studies revealed that both TEC and TYC are effective in surface modification, however, upon detailed surface analysis it was determined that TYC gave 20-80% higher surface coverage when compared with TEC .

## Future Plans

We aim to functionalize Si(111) surfaces using TYC and further carry out controlled radical polymerization to form fluoro-polymer onto reactive terminus of modified surfaces to improve surface properties for various applications.

## Acknowledgement

This project is funded by the Marie Curie Actions in collaboration with ASML.

## References

1. Massi, A.; Nanni, D., *org & Biomol Chem* **2012**, 10, 3791-3807
2. R. K. Iha, K. L. Wooley, A. M. Nystrom, D. J. Burke, M. J. Kade, C. J. Hawker *Chem. Rev.* **2009**, 109, 5620-5686
3. C. C. Albert N, S. Ciampi, J. B. Harper, J. J. Gooding *Surface Science* **2010**, 604, 1388-1394
4. M. A. Caipa Campos, J. M. J. Paulusse, H. Zuilhof *Chem. Commun.* **2010**, 46, 5512-5514
5. B. Lowe, C. E. Hoyle, C. N. Bowman *J. Mater. Chem.* **2010**, 20, 4745-4750
6. L. Scheres, M. Giesbers, H. Zuilhof *Langmuir* **2010**, 26, 10924-10929