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Q-Sense | [Application Note] 28

QCM-D to study photoresist dissolution

Photoresist polymers are commonly used in industrial processes such as micro-electronics and etching. They are light sensitive and are used where a patterned surface coating is desired. This study uses QCM-D to analyze properties of photoresist polymer films.

Introduction

Many newly developed photoresist polymers swell when exposed to the developing solution, which is used when creating a lithographic structure with photoresist polymers. For these polymers, the effects on the rate of dissolution due to the swelling process are poorly understood. The study reported in this application note explores the response of a thin film to an aqueous alkaline solution as a function of the composition of the polymer as it changes. The study was conducted in real time using Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). The reported data challenges the current models of photoresist polymer film dissolution mechanisms that do not take into account the swelling properties of the film.

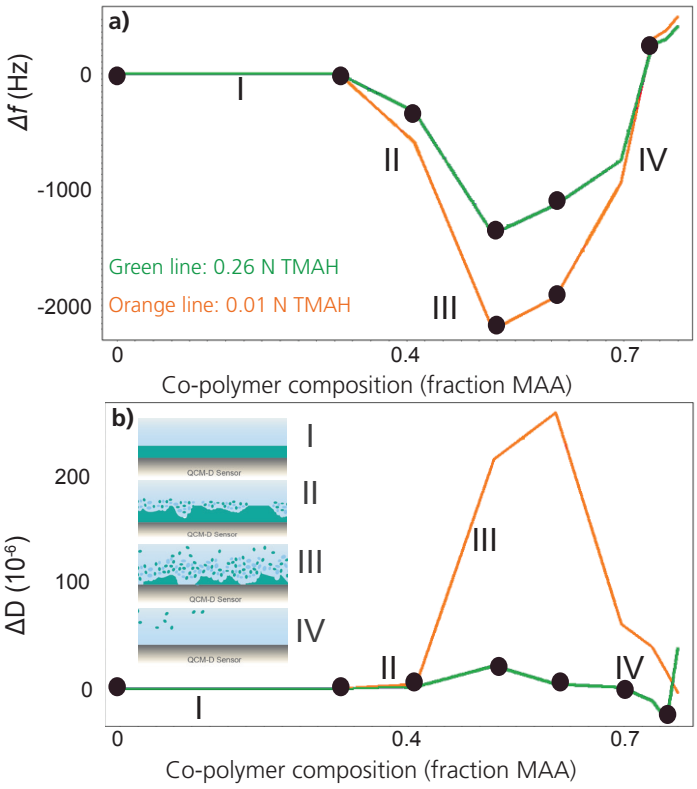
Experimental

Q-Sense silicon oxide (QSX 303) or chromium (QSX 315) sensors were subjected to silanization and then spin-coated with the photoresist polymer to 120 nm thickness. The polymer-coated sensors were then subjected to UV light to generate a photo acid catalyzed deprotection reaction, see schematic in Figure 2. This reaction transforms the hydrophobic polymer into a hydrophilic co-polymer matrix. The amount of co-polymer (abbreviated MAA) formed could hence be controlled, generating several different sensor surfaces with different fractions of co-polymer (fMAA).

To gain insight into how the different polymer coatings respond to the alkaline aqueous solution used in the development stage, the coated sensors were placed in a Q-Sense E4 measurement chamber and a tetramethylammonium hydroxide (TMAH) solution was injected. The mass change, uptake via film swelling, or release via film dissolution, was quantified from the change in frequency (Δf) and the change in dissipation (ΔD).

Results and discussion

Injection of the TMAH solution onto the sensors with different co-polymer compositions yielded varied responses in the QCM-D measurements. When the amount of co-polymer (fMAA) exceeded 0.3, an increase in mass (decrease in Δf) was observed



Green dots: dissolved polymers
Light blue: water-rich, swollen polymers

[Figure 1a and b]: illustrates the mass and viscoelastic changes with varying co-polymer composition upon TMAH injection. From these QCM-D data in combination with FTIR spectroscopy, the authors were able to identify four different regimes of how the thin film responded to the developing solution: (I) no swelling, (II) film swelling only, (III) swelling and partial film dissolution, and (IV) nearly complete film dissolution. The different regimes were attributed to local chemical heterogeneity of the polymer films. One reason for the observed chemical heterogeneity is that during the deprotection reaction an increased number of hydrophilic domains within the film are produced, leading to different surface morphologies. These hydrophilic nano-scale structures determine the degree of possible swelling and dissolution. Please note that the lines are only to guide the eye.

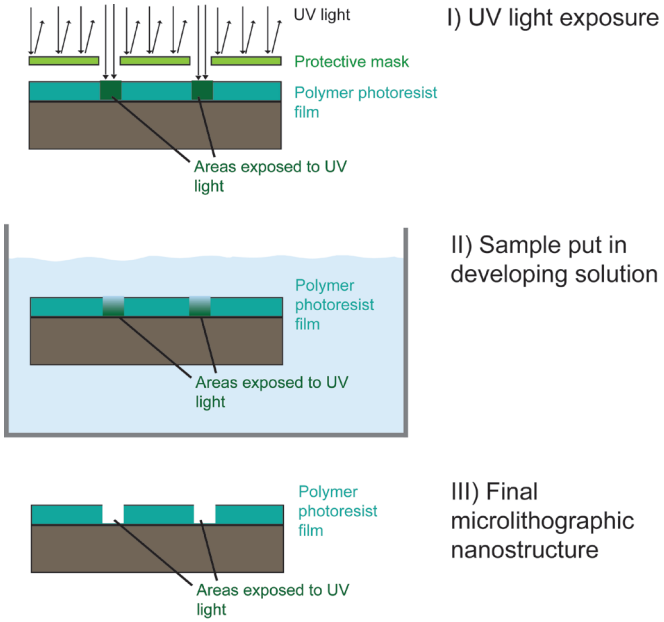
on the sensor surface. The mass increase was attributed to polymer film swelling upon addition of an alkaline solvent. Above an fMAA of 0.5, a loss of mass from the sensor (increase in Δf) was detected and interpreted as film dissolution. The softness (viscoelastic properties) of the film (ΔD) also varied with co-polymer content and swelling levels.

Conclusions

This application note highlights the use of QCM-D to analyze properties of photoresist polymer films. The study challenges the traditional understanding of photoresist dissolution and adds an additional level of complexity to these processes in terms of film swelling and partial dissolution. Photoresist polymers can successfully be coated onto a QCM-D sensor, allowing real-time analysis of the etching processes.

Acknowledgements

We thank Dr. Vivek Prabhu for valuable input in the preparation of this application note.



[Figure 2]: Principle of using photoresist polymers for patterned surfaces: The photoresist polymer is initially coated onto the entire surface of interest. The desired pattern is then transferred to the photoresist polymer layer by illuminating it through a photo mask (I). Illumination changes the properties of the polymer and allows for solubilization of the illuminated or non-illuminated sections, for positive and negative resist, respectively, in an aqueous developing solution (II). This generates microlithography structures on the surface (III). A typical etching process using photoresist polymers is illustrated here.

References:

1. Rao, A., Kang, S., Vogt, B.D., Prabhu, V. M., Lin, E.K., Wu, W., and Muthukumar, M. Effect of Deprotection Extent on Swelling and Dissolution Regimes of Thin Polymer Films. Langmuir 22, 10009-10015 (2006).

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