Optimization of Thermal Process Employed in Polymer Micromachines and Microlithography

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Abstract
In this work we present a study of the optimization of the thermal step employed during development of polymeric micromachine and microlithography processes. For this study three polymer types were utilized, based on Novolac and PMMA matrixes. These materials were analyzed by thermal analyses (DSC - Differential Scanning Calorimetry) and mechanical tests (mechanical stress was measurement by substrate curvature). With those analyses we can obtain a relationship between a glass transition and mechanical stress observed in polymer structures. With the analyses of the mechanical stress of the Novolac type polymers, it was possible to determine the incorporation of silicon in the polymeric layers in resists (silylation step) by measurement of the glass transition.

1. Introduction
In the process of micromachine fabrication the most important steps are the prebaking and postbaking of photoresist and polymers [1]. In many cases these steps can cause adhesion failure, pinholes problems and hillocks and increase to stress in the structures [2]. The influence caused by these steps stimulated the study of Tg (glass transition temperature) and Td (decomposition temperature) for this materials [4]. The Tg is usually determinated through thermal analyses generally using DSC (Differential Scanning Calorimetry) and mechanical tests (mechanical stress was measurement by substrate curvature). However, we can identify Tg by using the wafer curvature measurement equipment. In this case we have a glass transition determination in-situ. In this paper we demonstrate that the Tg of PMMA and photoresists could also be determined using Wafer Curvature Measurement (WCM) techniques and we compare with DSC thermal analyses. The silylation is a particular case of the Top Surface Imaging (TSI) process and involves the incorporation of silicon in a surface of polymer [6-7]. After the selective silicon incorporation, the polymeric film is submitted to an oxygen dry etching in order of obtain the final pattern.

2. Experimental
In our process we use three types of polymer matrixes Novolac: photoresists Tokyo Ohka OFPR 5000, All Resist AR-P 322 usually employed in microlithography and micromachining respectively and PMMA 2041 of Elvacite. The PMMA was made in two compositions: 10 and 20% wt diluted in MIBK (MethylIsobutylKetone) and xylene. The AR-P 322 is a positive tone resist and its thickness was 8 µm. The AFPR 5000 is a common photoresist for microlithography and its thickness is 2 µm. These polymers were deposited by a “spin coat” technique onto silicon wafers 3 inch, n type, (100). These wafers, before deposition, were cleaned with an RCA process [8]. The AR-P 322 was silylated, in this process silicon is incorporated in the polymer structure. This process was made using a solution: 70% xylene, 25% PGMEA and 5% HMCTS. The solution temperature was 40°C during 2 minutes.

In the first step we used a Tencor FLX 2410 equipment. The stress measurements were performed with different film thickness: 3 and 55 µm for PMMA 10 and 20% respectively. With the control program of the equipment we adjust the heating of 30 until 180ºC. In the other step the Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature of the various samples. The stress measurements were performed every 1ºC/min in a N2 ambient.

2.1. Tg determination with stress measurements
The Tencor system measure the changes in the radius of curvature of a substrate caused by the films deposited. The stress in the film is calculated from the radius of curvature of the substrate-using the following equation:

$$ \sigma = \frac{Er^2}{(1-\nu)6R}$$
Where, \( E / (1-\nu) \) is the biaxial elastic modulus of the substrate (1.805E11 Pa for (100) silicon wafers), \( h \) is the substrate thickness (m), \( t \) is the film thickness (m), \( R \) is the substrate radius of curvature (m) and \( \sigma \) is the average film stress (Pa). Figure 1 is a drawing of the substrate deformed to radius \( R \) by deposition of a film. In this case the film is under compression deforming the substrate.

**3. Results and Discussion**

Figure 2 presents the typical DSC curve of PMMA 2041 of Elvacite. The \( T_g \) values measured were 109\(^\circ\)C.

These studies were important for optimizing the thermal annealing in our process. The influence of this step in many cases can be observed in PMMA structures (Figures 5 and 6). These figures showed the influence of the thermal annealing in two cases, in PMMA polymer films and in tri-layer lithography structures.
These effects (shown in figures 5 and 6) are caused with increase of stress with temperature elevation during the micromachine fabrication. The same study was applied to two other photoresists (Novolac AR-P 322 and Tokyo Ohka OFPR 5000) and their stress-temperature curves are shown in figures 7 and 8. With both photoresists we can observe, during the heating of samples, stress relaxation when the Tg occurs. In DSC analyses the values of Tg observed were 81,45 and 85,46 °C for ARP 322 (All Resist) and OFPR 5000 (Tokyo Ohka) respectively. These values were confirmed with the Wafer Curvatures Technique (Figures 7 and 8). So with this technique it is possible to optimize the thermal process employed in microelectronics and minimize the stress effects.

With these studies we can optimize the thermal annealing applied to photoresists Novolac AR-P 322 employed in our process, avoid the cracks in these film as observed in figures 9.

Fig. 6: Cracks in try-layer structures of PMMA caused by thermal annealing.

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Fig. 7: Cracks in photoresist Novolac AR-P 322.

The Tg identification with the method of wafer curvature measurements allows us to conclude it was possible to identify the glass transition in a silylated structure. In this case we can observed that Tg changes value after the incorporation of silicon. The value observed was around 60°C (figure10). This is the result of the change in mobility of the polymer’s chains in function of the silicon molecule incorporation [9].

Fig. 9: Cracks in photoresist Novolac AR-P 322.

4. Conclusion

The use of wafer curvature measurements to infer the stress in films has been a versatile method for studying the mechanical behavior of organic coatings. This technique has the advantage that it is readily adapted to in situ measurements at elevated temperatures in conditions simulating actual processing environments. So it was possible to obtain the relationship with Tg and mechanical stress of some polymers. The Tg observed with this analysis wafer curvature were very similar to Tg temperatures previously measured using DSC.

Fig 10.: Stress versus Temperature of silylated ARP-322.
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