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The Influence of Thermal Annealing in Polymers Employed in Microelectronics

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In this work we presented the influence of the thermal treatments in polymer employed in microelectronics and Micro Electro Mechanical System (MEMS) process. The thermal steps can cause adhesion failure, pin holes problems, hillocks and increase of stress in the devices structures. We studied three polymers type based in Novolac and PMMA matrix. These materials was analyzed by technique analyze thermal DSC (Differential Scanning Calorimetry) and the stress mechanical was measurement by substrate curvature. With those analyses we can possible obtained a relationship by a polymer glass transition and mechanical stress observed in structures of microelectronics devices.

<u>Keywords</u> Polymers; MEMS; Microelectronics; Photoresist.

1. INTRODUCTION

In the process of micromachine fabrication the most important step are the prebaking and postbaking of photoresists and polymers [1]. In many cases these steps can cause adhesion failure, pinholes problems, hillocks and increase of stress in the structures [2]. The influence caused by these steps stimulated the study of TG (glass transition temperature) and Td (decomposition temperature) for these materials [4]. The Tg is usually determinate through thermal analyses generally using DSC (Differential Scanning Calorimetry). However, we can identify of Tg by using wafer curvature measurement equipment. In this case we have a glass transition determination in-situ. In this paper we demonstrated that the Tg of PMMA and photoresists could also be determinate using wafer curvature measurement (WCM) techniques and compares with DSC thermal analyses.

2. EXPERIMENTAL

In our process we use three types of polymers matrix: photoresists Novolac AR-P 322, Tokyo Ohka OFPR 5000 and PMMA 2041 of Elvacite. The PMMA was made in two-compositions: 10 and 20% wt, diluted in MIBK (MethylIsubutylKetone) and xylene. These polymers were deposited by "spin coat" technique onto silicon wafer 3 in, type n (100). These wafers, before deposition, were clean with a RCA step. In first step we used the equipment Tencor FLX 2410. The stress measurements were performed with different film thickness: 3 and 55μm for PMMA 10 and 20%wt respectively. The measurements of stress was realized every 1°C/min in an inert ambient (N₂) for 30 to 180°C range. In the other step the Differential Scanning Calorimetry (DSC) was used to determine the glass transition temperature of the various samples. This analysis was performed on DSC. The heating in DSC was 20°C/min in 30 to 160°C ranges.

Stress Measurements

The stress measurements the changes in the radius of curvature of a substrate caused by the films by deposited. The stress in the film is calculated from de radius of curvature of the substrate-using de following equation:

$$\sigma = Eh^2 / (1-v) 6Rt$$

Where, E / (1-v) 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), t is the substrate radius of curvature (m) and σ is the average film stress (Pa). The Figure 1 is a drawing of substrate deformed

to radius R by deposition of a film. In this case the film is under compression deforming the substrate.

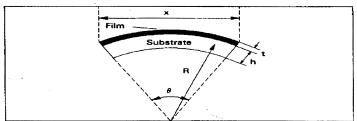


FIGURE 1 A substrate of thickness h, deformed to Radius R by deposited film

3. RESULTS AND DISCUSSION

The stress-temperature curves obtained for PMMA diluted in MIBK and xylene in two composition 10 and 20% wt are presented in figures 2 e 3. The values of Tg observed with both thicknesses were very similar to Tg temperature previously measured using DSC (around 109°C). In both cases we can observed, during the heating of samples, stress relaxation when the Tg occurs. This fact became more evidently near Tg of these materials. This occurs because segmental polymers motion. These segmental motions are favored by the large increase in chain mobility around Tg, when the material changes from the glassy to the rubbery or liquid state.

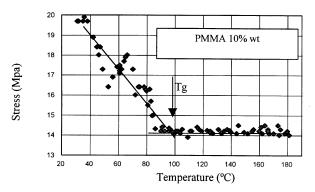


FIGURE 2 Stress versus Temperature of PMMA 10% wt

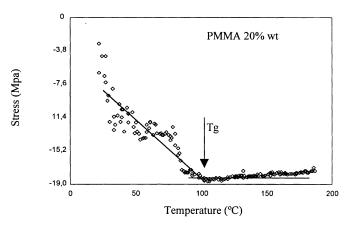


FIGURE 3 Stress versus Temperature of PMMA 20%

These studies were important for optimized the thermal annealing in our process. The influence of this step in many cases can be observed in PMMA structures. Figures 4 and 5.

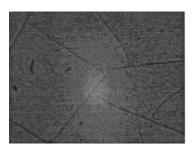


FIGURE 4 Cracks in PMMA in function thermal annealing.

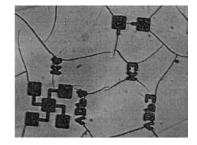


FIGURE 5 Cracks in try layer structures of PMMA in function thermal annealing.

The figures 4 and 5 shown the influence of the thermals annealing in two cases, in PMMA polymer films and in try-layer structures lithography. These effects are caused with increase of stress with

temperature elevation during the micromachine fabrication. The same study was applied with other two photoresists (Novolac AR-P 322 and Tokyo Ohka OFPR 5000) and their stress-temperature curves are shown in figures 6 and 7.

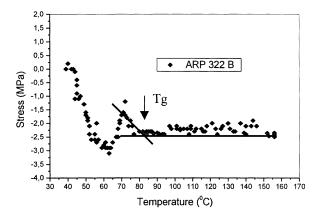


FIGURE 6 Stress versus Temperature of ARP-322

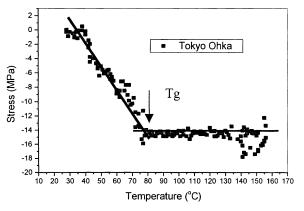


FIGURE 7 Stress versus Temperature of Tokyo Ohka

With both photoresists Figures 6 and 7 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 Wafer Curvatures Technique (Figures 6 and 7). So with this technique is possible optimize the thermal process employed in microelectronics and minimize the stress effects.

4. CONCLUSION

The use of wafer curvature measurements to infer the stress in films has been a versatile method for studding 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 was possible obtained 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.

ACKNOWLEDGMENTS

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