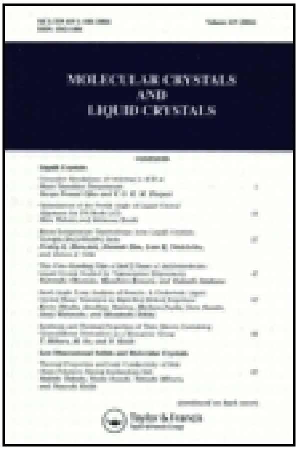

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Residual Stress Behavior in Methylsilsesquioxane-Based Dielectric Thin Films

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Residual Stress Behavior in Methylsilsesquioxane-Based Dielectric Thin Films

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Residual stress of methylsilsequioxane film, which was spin-coated on silicon substrate and followed by soft-baking, was measured *in-situ* during curing and subsequent cooling with varying processing conditions. The thickness and refractive index of the cured films were measured using ellipsometry. Their structure was also examined by X-ray diffraction.

Keywords: methylsilsesquioxane; thin film; low dielectric; residual stress; thermal stress; refractive index; crack; craze; X-ray diffraction

INTRODUCTION

Low dielectric interlayer (LDI) materials are highly demanded to provide dense wiring of metal conductor lines in compact size, consequently resulting in the fabrication of high performance integrated circuits [1-2]. Among a variety of candidate materials silsesquioxanes are very attractive LDI materials owing to their excellent thermal stability, film-forming processability, planarization, and gap filling properties. In this work, we chose methylsilsesquioxane (MSSQ) as an LDI material and studied in detail its residual stress behavior in thin film adhered on silicon substrates. In addition, its structure and refractive index were measured.

EXPERIMENTAL

MSSQ solutions with various concentrations in 5-methyl-2-pentanone (MIBK) were spin-cast on precleaned Si(100) wafers and subsequently soft-baked at 50°C for 9 hours in a nitrogen atmosphere: Here, MSSQ (GR650F grade) was received from Techneglas Inc. (USA) and its molecular weight was 10,000 <M_n>. Soft-baked MSSQ films were thermally cured in the hot-stage of a stress analyzer under nitrogen gas flow by various curing protocols over the range of 200-500°C. Residual stress in film generated during the curing process was measured *in-situ* as a function of temperature and time, using a residual stress analyzer[2-5]. Film structure was examined wide-angle X-ray diffraction (WAXD) using a Rigaku X-ray diffractometer (Model RINT-2500). The film thickness and refractive index were measured using a WVASE32 ellipsometer with a light source of 632.8 nm wavelength.

RESULTS AND DISCUSSION

As shown in Figure 1, soft-baked MSSQ films exhibited residual stress of 4-8 MPa at room temperature. In heating run, the residual stress was relaxed gradually with increasing temperature up to 60°C and then

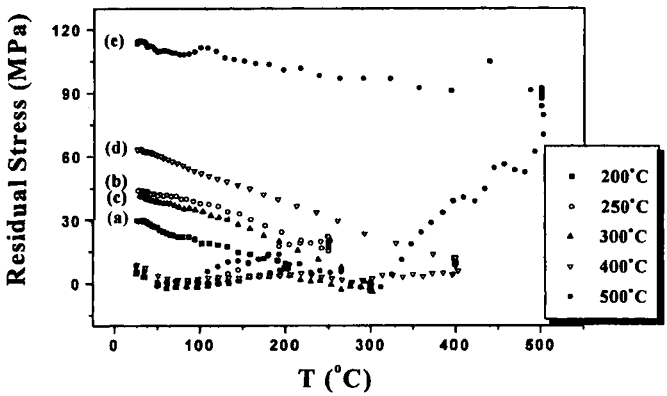

FIGURE 1. Residual stress-temperature profiles of MSSQ films measured *in-situ* during curing at various temperatures and subsequent cooling under N_2 gas flow: (a), 200°C/100 min; (b), 250°C/100 min; (c), 300°C/100 min; (d), 400°C/60 min; (e), 500°C/60 min. Here, both heating and cooling rate were 2.0 K/min. The thickness of films cured was ca. 1600 nm.

turned to build up slowly with increasing temperature from ca. 110°C. During subsequent cooling after cured at a chosen temperature, the stress increased almost linearly with descending temperature and finally reached to 30-115 MPa, depending on the curing temperature. Higher curing temperature generates higher residual stress in the film.

In particular, the film stress built during the curing process was apparently affected highly by all aspects related to the curing reaction: heating rate and step, byproducts and their removal, thermal expansion, and softening phenomenon (see Figure 2). In contrast, such influences in the stress due to the variations in the curing process were not reflected to the film stress generated during the subsequent cooling process. That is, the stress generated during cooling process after cure is not affected by both heating rate and step in the curing reaction if both final curing

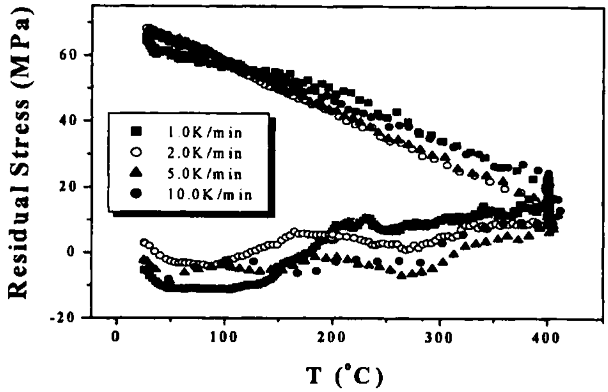

FIGURE 2. Effects of ramping rate and step variation on the residual stress of MSSQ films: ■, single-step cure (400°C/60 min); ▲, single-step cure; ●, single-step cure; O, two-step cure (200°C/30 min and 400°C/60 min). The thickness of films cured was ca. 1400 nm.

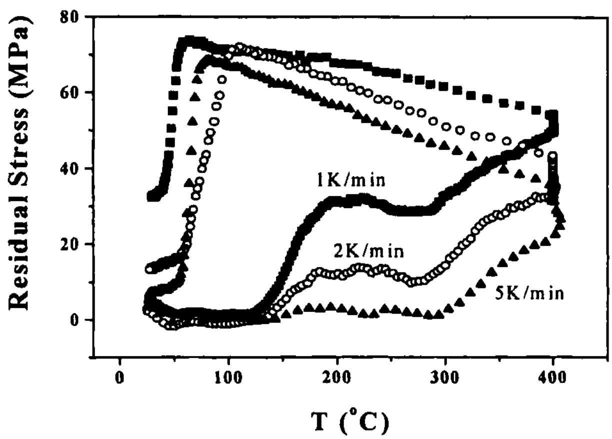

FIGURE 3. Effect of ramping rate on the residual stress of MSSQ films. All films were cured at 400°C for 60 min. The thickness of films cured was ca. 3700 nm.

temperature and film thickness are fixed. However, this statement is limited to thin MSSQ films which have a thickness less than a critical thickness, which is free from crack and craze. The MSSQ film was found to have a critical thickness of ca. 3000 nm. For example, Figure 3 shows residual stress profiles of relatively thick MSSQ films cured with various heating rates at 400°C. The heating rate affected residual stress in the film being cured and furthermore its effect was reflected to the stress generated during the subsequent cooling process. On cooling run the residual stress in each film dropped suddenly below 100°C. These stress drops are caused by cracks occurred in the film. Such cracks and their formation were confirmed by optical microscopy.

The refractive index (*n*) of cured MSSQ films were determined to be in a range of 1.380-1.405, depending on the curing temperature: higher curing temperature gave lower refractive index in the film. From the measured refractive index, the dielectric constant (ε) of MSSQ films is estimated to be 1.9044 - 1.9740 at an optical frequency of 632.8 nm (474.08 THz) using a simple Maxwell equation, $\varepsilon = n^2$.

Structural information in the cured films was obtained by WAXD. All the films exhibited two peaks which are very broad: one strong peak over 2-16° (2θ) and another weak peak over 16-30° (2θ). For the first peak its peak maximum was shifted to the low angle region as the film was cured at high temperature: That is, its *d*-spacing was varied from 8.6 Å for the 200°C cured film to 12.3 Å for the 500°C cured film. This first peak is believed to be originated from pores generated in the film. This is interpreted to be the interdistance between the centers of pores. The appearance of this peak indicates that such pores are closely packed each other in the film. The pores seem to generate in large size in case of curing at high temperature. The second peak centered at 22.5° is considered to be an amorphous halo in the film.

CONCLUSION

Structure and properties of MSSQ in films were evaluated as a LDI material candidate. Pore generation was detected in the cured film and the interdistance of pores was increased in case of curing at high temperature. The pore generation contributes to the lowering of dielectric constant in the cured film. The residual stress in the film, which is one of major critical parameters related to the reliability issues in multilayer microelectronic devices, was *in-situ* monitored during fabrication process. Overall, the residual stress generated in the film varied over a range of -3 MPa to 115 MPa, depending on the soft-baking, curing and cooling temperatures, and film thickness. The residual stress level and its variation are high enough to cause a serious crack and craze problem in the film itself and also interfacial failure in multilayer structure. Thus, one should carefully concern the residual stress and its associated reliability issues when the MSSQ material is considered as a LDI material candidate.

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