MECHANICAL PROPERTIES MEASUREMENT OF PECVD SILICON NITRIDE AFTER RAPID THERMAL ANNEALING USING NANOINDENTATION TECHNIQUE

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ABSTRACT
This paper investigated the residual stress, elastic modulus, hardness, and fracture toughness of PECVD silicon nitride films subjected to RTA processing between 200 and 800 °C. It was found that additional residual tensile stresses were generated during the RTA process and had a maximum value for a processing temperature of 400 °C. On the other hand, the nanoindentation testing revealed that both the modulus and hardness varied significantly with respect to RTA temperatures. Finally, the fracture toughness of the un-heat treated nitride was estimated as 1.33 MPa√m based on a series of Vickers micro-indentation tests. It was found that the RTA process would also enhance its fracture toughness. These results should be useful for MEMS or IC structure fabrication with the concerns of maintaining the structural integrity and improve fabrication performance in related applications.

Keywords: Silicon nitride, Nanoindentation, Rapid thermal process, Fracture toughness

I. INTRODUCTION
Plasma enhanced chemical vapour deposited (PECVD) silicon nitrides have been widely used in microelectromechanical systems (MEMS) and integrated circuits (IC) devices as a mask or barrier material. The mechanical properties of PECVD nitride subjected to thermal processing are traditionally important information for the device integrity [1,2]. However, their performance is largely determined by the residual stress generated during deposition and the after mentioned thermal processing. In addition, since PECVD process is usually performed at low temperature, it results in a porous microstructure. Such a microstructure could be densified after a mid-temperature (~ 400 - 600 °C) annealing but the densified process would accompany with a tensile stress generation and this would induce change in wafer warpage and possibly thin film cracking or delamination [2]. As a result, a fully understanding and detail characterizations on the stress behaviour of PECVD nitrides are required.

Thin film mechanical properties can be characterized via different tools. Recently, instrumentation micro- and nanoindentations, due to their nature of small size and relatively ease of specimen preparation, have been widely used for characterizing mechanical properties of micro- and nano-scale materials. By experiments, the applied load (i.e., F) and the penetration depth (i.e., d) can be simultaneously obtained. The F-d curve can be used to deduce the material hardness, yield strain, and Young’s modulus using the relation proposed by Oliver and Pharr [3,4]. However, that formula is primary used for bulk materials. For thin film attached on a substrate, that relationship should be modified. Using dimensional analysis originally proposed by Cheng and Cheng [5], in conjunction with finite element analyses, Chen developed a semi-analytical expression to address the substrate effect [6]. Based on Chen’s prediction, the F-d curve would depend on the modulus and thickness ratios between film and the corresponding substrate.

This paper mainly explores the thermo-mechanical behaviour of PECVD nitride films after rapid thermal annealing (RTA) at 200 – 800 °C using nanoindentation techniques. The F-d curves with different indentation depth would be observed for qualitatively verification of the relationship proposed by Chen [6]. Based on these F-d curves, the hardness and modulus of nitride after annealing can be determined. In addition, the fracture toughness of nitride would also be estimated via Vickers indentation crack propagation technique.
The rest of the article presents the characterization and the discussion of the test results in detail. In Section II, the fabrication of specimens and the preparation of the test plan are introduced. Detailed experimental characterizations are presented in Section III and followed by the results and discussions addressed in Section IV. Finally, Section V concludes this work.

II. SPECIMEN FABRICATION AND EXPERIMENT PREPARATION

The overall experimental flow is shown in Figure 1. 5000 Å PECVD nitrides were deposited on 4-inch silicon wafers using a Nano-Architect Research/BR-2000LL PECVD system at temperature between 250 and 400°C and a pressure of 5 Torrs based on the following reaction formula:

$$\text{SiH}_4(g) + \text{NH}_3(g) \xrightarrow{\text{RF N}_2 \text{H}_2 \text{Si H}_2 \text{Si N H}_2} \text{SiN}_x : \text{H}(s) + 3\text{H}_2(g)$$

After deposition, the wafers were die-sawed into square dies (10 mm × 10 mm). The initial curvatures were then inspected via a TENCOR INSTRUI/MA-1450 Profilometer. By Stoney formula [7], the residual stress, $\sigma$, can be further calculated as

$$\sigma = \frac{E_s h_f^2}{6(1-\nu_s) h_s R},$$

where $E_s/(1-\nu_s)$ is the biaxial modulus of substrate, $h_s$ and $h_f$ are the thickness of the substrate and the film, respectively. Finally, $R$ is the measured radius of curvature.

After inspection, specimens were then experienced rapid thermal annealing process using an Annealsys/AS-One 100 RTA system at temperatures of 200, 400, 600, and 800 °C and with an annealing period of 60 seconds. After the RTA process, the curvatures of the corresponding specimens were measured again to evaluate the residual stress generation using Eq.(1). Note that for extremely high stress state, Eq.(1) may not be proper and other modified formula should be used [8]. Meanwhile, the elastic moduli, as well as the hardness, of the nitride specimens were also characterized by a MTS Nano Indenter XP nanoindenter using a Berkovich indenter. A schematic plot of the nanoindentation test data is shown in Figure 2. By contact mechanics, it is possible to correlate the initial unload slope $S$ with the reduced elastic modulus $E_r$ as [3]

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A(h_s)}.$$

For Berkovich indenter, $\beta$ equals 1.034 and $E_r$ is defined as

$$\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_f^2}{E_f},$$

where the subscripts $i$ and $s$ represent the indenter and the substrate, respectively. As a result, once the modulus of the indenter is known, the plane strain modulus of the substrate can be deduced from the nanoindentation test data. In addition, the hardness, $H$, of the material can also be determined by dividing the maximum applied load with the maximum contact area.

Finally, a Vickers microindenter was also used to create initial cracks on square dies before and after RTA processing for evaluating the fracture toughness of the nitride films. If the strain energy release rate $G$ exceeds the critical strain energy rate $G_c$, cracks will propagated. As a result, it is possible to estimate $G_c$ using indentation experiments. The strain energy release rate for channelling cracking can be expressed as [9]

$$G = 1.976 \frac{(1-\nu_f)^2 h_f}{E_f},$$

where $\sigma$ is the applied stress, which equals residual stress in this case.
III. EXPERIMENTS

Residual Stress Variation

The residual stress variation with respect to RTP temperature was firstly characterized. Figure 3 shows the wafer profile before and after 600 °C RTA. The curvature increases significantly after RTA and this implies that the RTA process would induce additional tensile residual stress. A more complete characterization result is shown in Figure 4. Two trends are observed. First, film stress increases after RTA. That is, without RTA, the initial residual stress is approximate 1 GPa and it would increase to 1.5 – 2 GPa after RTA. Second, the change of stress increases with respect to RTA temperature until it reaches the peak at 400 °C and then gradually decreases.

Nanoindentation

The PECVD films were then characterized using nanoindentation. By setting the peak load at 30.8 mN under a force control configuration, the p-d curves were obtained. As shown in Figure 5, it can be found that the curvature of the p-d curves rises with the RTA temperature and this implies that the hardness of nitride increases with the RTA temperature. A more complete test plan was conducted by changing the peak loads. After data reduction using the formula proposed by Oliver and Pharr [3], the relationships between the mechanical properties (i.e., modulus and hardness) and RTA temperatures are summarized in Figure 6. It can be found that for RTA temperature below 400 °C, the modulus and hardness are not sensitive to the RTA temperature. On the other hand, once the RTA temperature exceeds 400 °C, both modulus and hardness increases significantly as RTA temperature increases. Nanoindentation tests indicate that the modulus of PECVD nitride is between 90 and 130 GPa before RTA (or RTA temperature below 400 °C) and it becomes 170 – 200 GPa after a 800 °C RTA. On the other hand, the corresponding hardness rises from 10 - 12 GPa to 17 - 21 GPa. However, it is also important to observe that the results are peak loading dependent and this could be attributed to the substrate effect. That is, as the peak penetration depth exceeds 1/10 of the film thickness, the effect of substrate become important and the formula proposed by Oliver and Pharr [3] cannot count this scenario. On the other hand, for too shallow indentation, the surface roughness distribution would also influence the result. Nevertheless, in this work we are interested in the general tendency, not the detail numerical calculation. As a result, although the detailed numerical values in both hardness and modulus need to be further clarified, the qualitative conclusion is clear.
Vickers Microindentation Testing

In order to characterize the fracture toughness of the silicon nitride films, the specimens were indented by Vickers microindentor before and after RTA with a load of 245 mN. Figure 7 shows a typical optical microscope image for a specimen without RTA. Some penny-shaped and channeling cracks occur around the indentor. Nevertheless, the channeling is stable. Those pre-indented specimens were then experienced RTA processing with various temperatures (200, 400, 600, and 800 °C) and the crack growth was re-examined. Figure 8 shows the optical microscope images and it indicates that unstable channeling occurs for all cases. On the other hand, the indentation after RTA shows different results. As shown in Figure 9, with a load of 490 mN, the Vickers indentation results in unstable channeling for specimens experienced with 200 and 400 °C RTA, while those specimens experienced 600 and 800 °C RTA process do not exhibit unstable crack propagation. As a result, the nitride after 600 °C RTA can be used to estimate the fracture toughness. By Eq.(4), using the following numbers: $\nu = 0.27$, $h_f = 5000 \text{ Å}$, $\sigma = 1.47 \text{ GPa}$, and $E_f = 90 \text{ GPa}$, the critical strain energy release rate $G_c$ is estimated as 17.3 J/m². In parallel, by using the method proposed by Marshall and Lawn [10], the fracture toughness can be estimated via Vickers indentation test as

$$K_{xc}^* = 0.016 \left( \frac{E_f}{H} \right)^{1/2} \left( \frac{P_{\text{max}}}{c^{1/2}} \right),$$

where $E_f$ (90 GPa) and $H$ (11 GPa) are the modulus and hardness of the film, $P_{\text{max}}$ (245 mN) is the indentation lading and $c$ the crack length. By Eq.(5), the $K_{IC}$ of nitride prior to RTA is estimated as 1.33 MPa√m.

Figure 3. Surface profile of nitrides before and after RTA process at 600°C.

Figure 4. Changes in curvature of nitrides before and after various RTA processes.
Figure 5. Load-depth curves of nanoindentation on PECVD silicon nitrides after various RTA processes.

Figure 6. The relationship between (a) elastic modulus and (b) hardness with respect to RTA temperature at different peak load of nanoindentation.
Figure 7. Optical image of Vickers micro indentation with a load of 245 mN.

Figure 8. Optical images of crack propagation for pre-indentated specimens after RTA.

Figure 9. Optical images of crack propagation for specimens indented after RTA.
IV. DISCUSSION

Residual stress calculation and the relationship between stress and RTA temperature

PECVD films, due to its low temperature deposition, usually have porous microstructure. Once they experience higher temperature annealing (e.g., 400 °C), the increased mobility tends to drive the molecules to move for reducing the micro voids. As a result, the average molecule distance increases and this represents a net increase in residual tensile stress. However, for further increasing in annealing temperature (e.g., up to 600 – 800 °C), the stress relaxation and plasticity of the substrate become important (silicon has a transition temperature around 600 °C [11]) and the overall film residual stress would not be as high as the case for 400 °C RTA.

Nanoindentation data, hardness & modulus vs. RTA temperature

The modulus of single crystal silicon is well characterized as 160 – 170 GPa, which is larger than the modulus of the PECVD nitride prior to RTA (or RTA temperature below 400 °C) and is slightly smaller than the nitride after a higher temperature RTA processing. As a result, both the soft film/hard substrate and hard film/soft substrate (based on the modulus ratio) combination occur in this test. According to the numerical investigation [6], the substrate effect also depends on the modulus ratio. In particular, the accuracy of the original nanoindentation formula would drop significantly for the hard film/soft substrate case. This would be a concern for a more accurate determination of material properties in the future.

Strain energy release rate and $K_{IC}$ calculation

The fracture toughness of brittle ceramics such as silicones, oxides, and nitrides is around 1 MPa$\sqrt{m}$. Therefore, the estimated fracture toughness 1.33 MPa$\sqrt{m}$ is reasonable. By cross-evaluating the information of residual stress measurement, the first set of the Vickers indentation data (indenting before RTA), and the second set of the Vickers indentation data (indenting after RTA), it is reasonable to conclude that the channeling process occurs before reaching the final RTA temperature. By the information of the film stress measurement and the second set of the Vickers indentation data, it is believe that the RTA process would improve the fracture toughness. That is, although the residual stress of the 600 °C RTA processed nitride is higher than the nitride after 200 °C RTA processing, it results a stable channeling process.

Finally, it must be pointed out here that since only four RTA temperatures are selected, some temperature-specified conclusion of this work (e.g., maximum tensile stress generated, transition temperature, etc) may vary once a more detailed characterization (i.e., using more RTA temperatures) is conducted. Nevertheless, the general tendencies and trends obtained from this work, in together with the fracture toughness test data, still provide very useful information for related MEMS and IC structure integrity design applications.

V. SUMMARY AND CONCLUSION

This paper investigates the residual stress, modulus, hardness, and fracture toughness of PECVD silicon nitride films subjected to RTA processing between 200 and 800 °C. The as fabricated residual tensile stress was approximately 1 GPa and the additional residual tensile stresses were generated during the RTA process. For example, after 400 °C RTA, the tensile stress was increased to 1.5 - 2 GPa. On the other hand, the nanoindentation testing revealed that both the modulus and hardness varied significantly with respect to RTA temperatures. The modulus varied from 90 to 200 GPa and the hardness increased from 10 GPa to 20 GPa. Finally, the fracture toughness of the un-heat treated nitride was estimated as 1.33 MPa$\sqrt{m}$ based on a series of Vickers micro-indentation test. It was found that the RTA process would also enhance its fracture toughness. These results would be useful for related MEMS or IC structure fabrication for the concerns of maintaining the structural integrity and improve fabrication performance in related applications.

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References