Stress Analysis in Silicon Substrates during Thermal Oxidation*

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The stress development mechanism during local thermal oxidation of a silicon substrate is discussed based on the predicted results using a two-dimensional thermal oxidation process simulation program OXSIM2D developed by the authors. Predicted stress change during the oxidation agrees well with the measured data obtained by means of micro-Raman spectroscopy. There are three main factors which play important roles in stress development in the newly grown oxide film and the substrate. They are the volume expansion of the oxide film, the viscosity of the oxide film, and the bending of the silicon nitride film which is used as the oxidation barrier. These factors give rise to the complicated stress distribution and the stress change near the edge of the nitride film during thermal oxidation.

Key Words: Structural Analysis, Viscoelasticity, Thermal Oxidation, LOCOS, Raman Spectroscopy

1. Introduction

LSI's (Large-Scale Integrated devices), such as DRAM (Dynamic Random Access Memory), consist of many metal and insulation films on silicon substrates. LSI's are fabricated by thin-film deposition processes using PVD (Physical Vapor Deposition) and CVD (Chemical Vapor Deposition), partial film etching processes and high-temperature annealing processes for film stabilization. If excess stresses are generated during these processes, dislocations sometimes occur in the silicon substrate⁽¹⁾. These dislocations are caused by a deterioration of electric characteristics such as current leakage. Additionally, these stresses appear to affect the electric characteristics directly⁽²⁾, even if the dislocations do not occur. Thus, the evaluation of these stresses in a silicon substrate is important in maintaining the high reliability of LSI's.

There are two main stress development mechanisms in LSI devices during the fabrication process. One is thermal stress caused by the difference in thermal expansion coefficient between the substrate and the thin films, and the other is the intrinsic stress which is generated during deposition processes. The thermal oxidation process generates the biggest intrinsic stress⁽³⁾ among the fabrication processes. In the oxidation process, silicon substrates are exposed to a high-temperature oxidation atmosphere and silicon dioxide (SiO_2) is formed on the silicon substrate. One of the main purposes of the process is the formation of device isolation structures on the surface of silicon substrate.

The LOCOS (Local Oxidation of Silicon) structure is the most popular isolation structure for an LSI device. The fabrication process of LOCOS is shown in Fig. 1. The silicon substrate is first covered with an oxidation-proof mask (silicon nitride thin film) about 100 nm thick. Sometimes, the underside of the mask is coated with a very thin SiO_2 film (pad SiO_2) to avoid dislocation generation. Next, the mask of device isolation fields is removed and exposed to an oxidation atmosphere (H_2O or O_2 atmosphere) at high

* Received 2nd March, 1995. Japanese original: Trans. Jpn. Soc. Mech. Eng., Vol. 60, No. 571, A (1994), pp. 805-810. (Received 27th May, 1993)

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temperatures, up to 1100°C. Then, SiO₂ films about 300 nm thick are formed on the silicon substrate. During the oxidation reaction, a large volume expansion of about 125 percent occurs, leading to the projection of SiO₂ films from the silicon substrate surface. As the oxidizing species diffuse into the pad SiO₂ and invade into the bottom of the mask, the silicon substrate under the mask edge is oxidized, and the SiO₂ film assumes the shape of bird's beak at the mask edge. It is necessary to suppress the bird's beak in order to maintain sufficient transistor (active) area for highly integrated devices. On the other hand, it is known that a short bird's beak process tends to generate dislocation during oxidation⁽⁴⁾. Thus, not only a dislocation-free process but a short bird's beak process is desirable.

It is known that the silicon oxidation reaction has mechanical stress dependence⁽⁵⁾, and stress distribu-

tion changes the shape of the SiO₂ thin film. Therefore, it is necessary to analyze the oxidation reaction and stress generation at the same time to predict SiO₂ film shape. We have developed a two-dimensional thermal oxidation process simulation program OXSIM2D⁽⁶⁾ which can analyze the shape of SiO₂ and stresses of the device structure. We have confirmed the accuracy of the SiO₂ shape prediction⁽⁷⁾⁻⁽⁹⁾. We have also revealed that Raman spectroscopy is effective for measuring the stress distributions in silicon substrate⁽¹⁰⁾, and applied the technique for measuring stress after thermal oxidation⁽¹¹⁾.

First, the accuracy of the program is discussed by comparing predicted stresses and measured results. Second, the stress development mechanism during thermal oxidation is discussed using simulation data.

2. Analysis Method of OXSIM2D

The process of the oxidation reaction was confirmed as follows by means of an experiment using an O¹⁸ tracer technique⁽¹²⁾.

(1) The oxidizing species in the atmosphere invade the interstices of the SiO₂ molecule at the SiO₂ film surface.

(2) The oxidizing species diffuse into the SiO₂ film and reach the Si/SiO₂ boundary.

(3) They react with the silicon at the Si/SiO₂ boundary and 125 percent volume expansion is generated.

Taking into account these reaction processes, OXSIM2D performs three steps as shown in Fig. 2. First, it analyzes the diffusion of the oxidizing species into the SiO₂ film by means of the diffusion equation under a quasi-static state. Then, it calculates the amount of silicon consumed according to the concentration of the oxidizing species at the Si/SiO₂ boundary, moving the boundary depending on the consumption. Finally, it supplies volume expansion strain to the transition region and analyzes the stress distribution in the total isolation structure. OXSIM2D repeats these three steps until the desired SiO₂

Fig. 1 Fabrication process of LOCOS

Fig. 2 Numerical model in OXSIM2D

thickness is attained. At this point, it can analyze the final shape of the SiO₂ film and the stress distribution.

The stress dependence on the oxidation reaction⁽⁵⁾ is also considered in the analysis to improve accuracy. The diffusion coefficient in SiO₂ film and reaction coefficients at the Si/SiO₂ boundary are determined by means of Kao's models⁽¹³⁾ as follows.

(1) Diffusion of oxidizing species is suppressed depending on the compressive stress of the SiO₂ film.

(2) The oxidizing reaction is suppressed depending on the compressive stress of the Si/SiO₂ boundary.

OXSIM2D adopts viscoelastic stress analysis to analyze high-temperature SiO₂ behavior. The constitutive equation and the diffusion equation are numerically solved using a finite element method with 4-node quadrilateral elements. The movement of the Si/SiO₂ boundary is realized by the boundary-fitted coordinate transformation technique⁽⁶⁾.

3. Results of Stress Analysis and Its Accuracy Evaluation

3.1 Simulation results of LOCOS structure

The simulated LOCOS structures are as follows. The mask is 0.15 μm thick and 1.0 μm wide. The pad SiO₂ is 0.03 μm thick and the oxidation temperature is 1 000°C. LOCOS thicknesses are 0.1 μm , 0.3 μm , 0.7 μm , and 1.0 μm . The Young's modulus E and Poisson's ratio ν used in the analysis were determined from previously reported values⁽⁶⁾ such that $E_{\text{Si}}=1.5 \times 10^5$ MPa, $\nu_{\text{Si}}=0.2$, $E_{\text{SiO}_2}=7 \times 10^4$ MPa, $\nu_{\text{SiO}_2}=0.17$, $E_{\text{SiN}}=3 \times 10^5$ MPa, and $\nu_{\text{SiN}}=0.3$. To obtain the results at room temperature, thermal stresses between oxidation temperature and room temperature were calculated after oxidation expansion.

The distributions of the normal stress component (σ_x) which is parallel to the silicon substrate surface are shown in Fig. 3. There are two stress distributions in SiO₂ films. One is tensile stress distribution under the center of the mask and the other is strong compressive stress distribution under the mask edge. In the early stage of oxidation, these stresses increase

with the SiO₂ film growth. However, at the final stage when SiO₂ film thickness is 1.0 μm , these stresses gradually decrease.

On the other hand, in the silicon substrate, there are three stress distributions, i.e., strong tensile stress under the center of the mask, weak compressive stress below the strong tensile stress under the mask, and compressive stress under the mask edge. In the early stage of oxidation, these stresses increase similarly to the stresses in SiO₂ film. As the SiO₂ film grows, the compressive stress under the mask edge decreases gradually, and the tensile stress under the center of the mask changes into weak compressive stress.

The distributions of the normal stress component (σ_y) which is perpendicular to the silicon substrate surface are shown in Fig. 4. In the SiO₂ film, there are two stress distributions, similarly to σ_x ; i.e., strong tensile stress under the center of the mask and compressive stress under the mask edge. The stress change during oxidation is also the same as σ_x .

In the silicon substrate, there are two stress distributions unlike σ_x ; i.e., strong tensile stress under the center of the mask and compressive stress under the mask edge. In the early stage, these stresses increase the same as σ_x . These stresses decrease gradually as the SiO₂ film grows, but stress change from tensile to compressive cannot be seen.

3.2 Comparison between analysis and measurement

3.2.1 Experiments The stress measurement data of the silicon substrate obtained by micro-Raman spectroscopy and analysis are compared in order to investigate the accuracy of the analysis. Since the shift of inelastic scattering light spectrum is proportional to the strain, the stress value can be measured using the method. The Ar⁺ laser is irradiated onto the silicon surface and the scattered light is detected by a JOBIN YBON U-1000 photon multiplier. Raman spectra are measured in the backscattering configuration using the 514.5 nm line of an argon ion laser. The scattered light is polarized in

Fig. 3 Oxide thickness dependence for stress distribution (σ_x)

Fig. 4 Oxide thickness dependence for stress distribution (σ_y)

Fig. 5 Cross-sectional stress measurement of LOCOS structure

order to measure the stress along a certain direction. The spot size of the laser beam is approximately $0.8 \mu\text{m}$. The stress value is calculated by the frequency difference between measured Raman spectra of the specimen and those of stress-free silicon⁽¹¹⁾.

The specimen size and structure are the same as in the analysis examples, and are as follows: pad-SiO₂ thickness of $0.03 \mu\text{m}$, mask thickness of $0.15 \mu\text{m}$, mask width of $1.0 \mu\text{m}$, and oxidation temperature of 1000°C .

3.2.2 Cross-sectional stress measurement in LOCOS structure The laser beam is irradiated to the cross section of the LOCOS structure and the stresses σ_x , which are parallel to the silicon substrate surface, are measured as shown in Fig. 5. The stress distributions in $0.3 \mu\text{m}$ -thick and $1.0 \mu\text{m}$ -thick LOCOS structures are shown in Figs. 6 and 7, respectively. The oblique lines indicate the probed regions and the values indicated are the measured data. It is considered that those values indicate the average stresses in those regions. In the early stage where thickness is $0.3 \mu\text{m}$ both the strong tensile stress 120 MPa under the mask and the compressive stress -50 MPa at the mask edge are detected in silicon substrate, as shown in Fig. 6. However, these stresses change into weak wide compressive stresses at the final stage when thickness is $1.0 \mu\text{m}$. These stress changes agree qualitatively with the analysis results of Fig. 3.

Fig. 6 Stress distribution in LOCOS structure (oxide thickness: $0.3 \mu\text{m}$)

Fig. 7 Stress distribution in LOCOS structure (oxide thickness: $1.0 \mu\text{m}$)

3.2.3 Surface stress measurement of LOCOS structure

The cross-sectional stress measurement is not quantitatively accurate because the stress relaxation that accompanies the cleavage of the silicon substrate cannot be taken into consideration. Therefore, surface stress measurement, in which the laser beam irradiated to the surface of the silicon substrate, is performed in order to obtain qualitative results. As the laser beam penetrates the mask, the stress under the mask can be measured as shown in Fig. 3. Since the laser beam penetrates to about $0.5 \mu\text{m}$ below the

Fig. 8 Surface stress measurement of LOCOS structure

Fig. 9 Average stress change under nitride mask

silicon surface, it is considered that the measurement data show the average value of the cylindrical volume from the surface to a depth of $0.5\ \mu\text{m}$. Then, the simulated results are converted to the volume average value and shown in Fig. 9 as predicted stress data. The stress under the mask increases at the early stage and changes into compressive stress at the final stage. The stress change tendency is the same as the results of the cross-sectional measurement data. The measured data agree well with the simulated results for every SiO_2 thickness, indicating the accuracy of the analysis.

4. Stress Generation Mechanisms during Thermal Oxidation

As the accuracy of the analysis is confirmed in Section 3, the stress generation for the LOCOS oxidation can be discussed using the analytical data. This discussion is divided into two parts. One is the early stage (SiO_2 thickness of $0.1\ \mu\text{m}$ to $0.7\ \mu\text{m}$). At this stage, stress generation due to the oxidation reaction overcomes the stress relaxation of SiO_2 . The other is the final stage (SiO_2 thickness of $0.7\ \mu\text{m}$ to $1.0\ \mu\text{m}$). Stress generation declines and the stress relaxation of the SiO_2 becomes dominant.

4.1 The early stage (SiO_2 thickness of $0.1\ \mu\text{m}$ to $0.7\ \mu\text{m}$)

4.1.1 Stress change in SiO_2 film The thickness of the SiO_2 film increases rapidly in the early

stage and this lifts up the mask edge as shown in Figs. 3, and 4. Because of this bending stress, compressive stress is generated under the mask edge in the Y direction. Since the SiO_2 film growth is restricted under the mask, a constricted part of the film is generated under the mask edge. This constricted part of the film disturbs the X -direction expansion of the SiO_2 film, leading to the generation of compressive stress under the mask edge. Since these compressive stresses in the SiO_2 under the mask edge disturb the diffusion of the oxidizing species as a bottleneck, the SiO_2 film growth under the mask is disturbed. This creates greater nonuniforming of the SiO_2 thickness and greater degree of mask bending. This mask bending increases the compressive stress and disturbs the SiO_2 film growth under the mask even more. Thus, this negative feedback makes these stresses increase rapidly as shown in Figs. 3, and 4.

On the other hand, tensile stress is generated in the back surface of the mask as the mask bends. Because of this tensile stress of the mask, tensile stress (σ_x) is generated in the SiO_2 film under the center of the mask. Tensile stress (σ_y) is also generated in the SiO_2 film under the center of the mask because of the bending stress of the mask.

4.1.2 The stress change in silicon substrate

Under the center of the mask, tensile stress like that in the SiO_2 film is generated because of the bending stress of the mask, and this stress increases with the degree of the mask bending.

A compressive stress is generated under the mask edge. As the Si/SiO_2 boundary shape is curved under the mask edge, the volume expansion of the corners interferes with each other and this generates compressive stress under the mask edge.

Another compressive stress (σ_x) is generated underneath the mask. According to the increase in nonuniforming of the SiO_2 film thickness, the gradual protrusion of silicon under the mask occurs. The silicon protrusion part is compressed by the SiO_2 film because of volume expansion during thermal oxidation and the compressive stress is generated.

4.2 The final stage of oxidation (SiO_2 thickness of $0.7\ \mu\text{m}$ to $1.0\ \mu\text{m}$)

4.2.1 The stress change in SiO_2 film Although the SiO_2 growth rate is controlled by the oxidation reaction rate at the Si/SiO_2 boundary in the early stage of oxidation, the growth rate is controlled by the diffusion rate of the oxidizing species in the final stage and the growth rate decreases gradually. As a result, the stress relaxation caused by the SiO_2 viscosity dominates the stress increase caused by volume expansion⁽¹⁴⁾ and the compressive stress at the mask edge decays. This decay makes the oxidizing

diffusion easy at the mask edge and the SiO₂ under the mask grows rapidly. The SiO₂ growth under the mask reduces the degree of the mask bending. Furthermore, the SiO₂ growth causes the stress relaxation of the SiO₂ under the mask. As a result, the tensile stress under the mask edge decreases rapidly.

4.2.2 The stress change in silicon substrate

According to the SiO₂ growth under the mask, the curvature of the Si/SiO₂ boundary under the mask edge becomes smaller. Since this makes the interference of volume expansion at the curve smaller, the compressive stress is decreased.

The tensile stress under the mask caused by bending of the mask is reduced in the same manner as the SiO₂ film stress change. As a result, the compressive stress underneath the mask becomes superior to the tensile stress under the mask. Finally, the silicon substrate under the mask is covered with a compressive stress field as shown in Fig. 7.

5. Conclusion

The stress analysis of the LOCOS structure was performed by means of the two-dimensional thermal oxidation process simulation program OXSIM2D. The analytical values were confirmed by the stress data measured by Raman spectroscopy. From these stress distributions, the following conclusions were obtained.

(1) The shape of the SiO₂ film and stress distributions during thermal oxidation depend on three factors: stress generation caused by volume expansion, stress relaxation caused by SiO₂ viscosity, and stress generation caused by the mask bending.

(2) Although the stress under the mask, which is parallel to the silicon substrate surface, is tensile at the early stage of oxidation, it changes gradually into

compressive stress with SiO₂ growth. The tensile stress caused by bending of the mask is superior at the early stage. On the other hand, the tensile stress is reduced because of the SiO₂ growth under the mask and finally the compressive stress becomes greater. The compressive stress is derived from the compression of the silicon protrusion part under the mask.

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