Effect of Phosphorus Doping on Crystallization-Induced Stress of Silicon Thin Films*

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The effect of phosphorus doping on the crystallization-induced stress of silicon thin films is discussed experimentally. Amorphous silicon thin films are deposited on thermally-oxidized silicon substrates using chemical vapor deposition. Phosphorus is doped to the film during film deposition using PH_3 gas. The initial residual stress of the phosphorus doped films is constant at -200 MPa, regardless of dopant concentration. The internal stress of the films changes to a tensile stress of 800 MPa during crystallization due to film shrinkage. Although the magnitude of the stress change is independent of the dopant concentration, the crystallization temperature of the film decreases with an increase of dopant concentration. The doped phosphorus at the film/substrate interface affects the crystallization process, i.e., the structure and crystallinity of the silicon thin films. The surface condition of the substrate also affects the crystallinity and crystallization-induced stress of the film.

Key Words: Experimental Stress Analysis, Residual Stress, Thin Film, Amorphous Silicon, Crystallization

1. Introduction

Thin film materials have been widely used in semiconductor devices. With the trend toward higher integration of devices, the device structure has had to become not only smaller but also more complicated. Also, to improve electronic performance of the devices, the number of thin film materials has steadily been increased. These structural changes cause stress to increase in the structure of the device as a result of thermal stress. This is due to mismatch in thermal expansion coefficients among different thin film materials and due to the high density of stress-concentrated corners. This stress increase sometimes gives rise to mechanical failure during the development of

new products. Typical failures are delamination and the cracking of thin films and dislocations in single-crystal substrates. Electronic failures such as device characteristic shift due to changes in the energy band gap of the semiconductor or due to the piezoresistance effect are also caused by mechanical stress. It has, therefore, become increasingly important to optimize the mechanical stress field in the structure of the device to improve the reliability of semiconductor devices and reduce their development costs⁽¹⁾⁻⁽⁵⁾.

The important stress development process in thin film materials is not only thermal stress but also the intrinsic stress of films which occurs during film deposition due to thermodynamically non-equilibrium atomic bonding. This intrinsic stress strongly depends on film deposition conditions such as temperature and gas pressure. To date, it has been very difficult to predict intrinsic stress precisely, because the formation process for atomic bonding in thin films during film deposition cannot be analyzed. Thus, intrinsic stress in films used for products must be determined experimentally⁽⁶⁾.

To discuss the stress-development process in thin films further, volumetric change of films during phase

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transition also has to be considered. For example, silicon thin films shrink by about 0.6% during crystallization. This shrinkage causes a tensile stress of about 1 000 MPa in the film because free shrinkage is restricted by the substrate⁽⁷⁾⁻⁽⁹⁾. This stress change occurs at a crystallization temperature of about 600°C. Since the strength of silicon decreases drastically at high temperatures above 600°C, such a high stress may cause dislocation in the single crystal substrate, which greatly reduces the reliability of the device.

Since silicon is a semiconductor material, impurities such as boron or phosphorus are doped in silicon substrates to electrically activate them. When amorphous silicon thin film is deposited, the impurity is doped during film deposition using dopant gas. If the doped-impurity affects the crystallization process of a silicon thin film, the internal stress of the film may also change. Thus, in this report, the effect of phosphorus doping in silicon thin films on the crystallization process and crystallization-induced stress of the films is discussed experimentally.

2. Experimental Method

The change in the internal stress of thin films was determined by measuring the deflection of the film deposited substrates. Amorphous silicon thin films were deposited at 525°C on thermally oxidized (001) single crystalline silicon wafers, about 10 cm in diameter and 0.55 mm in thickness, by chemical vapor deposition using Si₂H₆ gas. The thickness of the deposited film was about 550 nm. The measurement samples were cut from the film-deposited wafers into strips, about 30 mm long and 5 mm wide. The deflection of the sample was measured along the longitudinal direction of the strip, as shown in Fig. 1. Assuming uniform film stress, the internal stress of the film was determined by the following equation.

$$\sigma_f = 4E_s(t_s)^2\delta / \{3(1-\nu_s)t_fL^2\} \quad (1)$$

Here, E_s , ν_s are Young's modulus and Poisson's ratio of the substrate, t_s and t_f are thicknesses of substrate (s) and film (f), L is measurement length and δ is deflection of the substrate, respectively. Since the

Fig. 1 Stress measurement method for thin films

longitudinal direction of the sample was parallel to the <011> crystallographic direction of silicon, E_s , ν_s in this report were about 170 GPa and 0.07, respectively. The deflection of the sample placed in an infrared furnace was measured using a scanning laser microscope operating through a quartz window. The resolution of the deflection measurement was about 0.1 μ m, when an Ar-ion laser with a 488 nm wavelength was used. By substituting these values into Eq.(1), the stress measurement resolution was determined to be about 15 MPa. The sample was annealed in flowing argon gas for 30 minutes at temperatures from 400°C to 900°C.

Since the calculated stress only indicates the residual stress at the measurement temperature, it is important to separate thermal stress from intrinsic stress or the crystallization-induced stress of silicon thin films. In this report, it was confirmed by measuring the deflection of the crystallized sample that the deflection of the sample due to thermal stress was within experimental error. Therefore, we assumed that the measured stress change in silicon thin films was determined by a combination of the intrinsic stress of amorphous silicon films, crystallization-induced stress and stress relaxation due to the viscoelasticity of silicon films.

3. Internal Stress Change in Silicon Films during Annealing

The annealing temperature dependence of internal stress in phosphorus-doped silicon thin films is shown in Fig. 2. The dopant concentration was varied from 0 to $4 \times 10^{20}/\text{cm}^3$. The initial residual stress of the amorphous film without doping was a compressive stress of about 200 MPa. This internal stress field did not change very much even when the film was heated to 600°C. Crystallization of the film started at about 630°C. During crystallization, tensile stress of about 1 000 MPa developed due to film shrinkage. Thus, the

Fig. 2 Annealing temperature dependence of internal stress in phosphorus-doped silicon thin films

residual stress in the film reached a tensile stress of about 800 MPa at 650°C. The developed stress relaxed during annealing at temperatures above 700°C. This stress relaxation occurred mainly as a result of the viscoelasticity or plasticity of the film.

The initial residual stress of phosphorus-doped amorphous silicon films was almost constant at about 200 MPa, regardless of the dopant concentration. The initial stress of these films also showed almost no change during annealing up to 550°C. However, the crystallization temperature of phosphorus-doped films decreased from 630°C to 580°C as the dopant concentration increased. The magnitude of the change in the internal stress during crystallization was almost constant at 1 000 MPa, as it was during crystallization of the film without doping. The residual stress of all films just after crystallization was a tensile stress of about 800 MPa. The shrink rate of the films during crystallization was almost constant at about 0.6%, regardless of the dopant concentration. Remarkable change was observed in the stress relaxation process in phosphorus-doped films during annealing above 800°C. The stress relaxation rate of the films increased with increase in dopant concentration. The final residual stress of the film without doping after 900°C annealing was about 500 MPa. It was about 450 MPa when doped with phosphorus of about $1 \times 10^{20}/\text{cm}^3$, while it decreased to about 250 MPa when doped with phosphorus of about $4 \times 10^{20}/\text{cm}^3$. The reason for the high stress relaxation rate in phosphorus-doped film is not clear. The doped phosphorus may activate viscoelasticity or plasticity in the film. The effect of phosphorus doping on the stress

relaxation process in silicon thin films is an open question needing clarification.

Since the strength of silicon decreases drastically at high temperatures above 600°C⁽⁵⁾, such high stress may cause dislocation in the single crystal substrate, which greatly reduces device reliability. Thus, it is very important to understand the crystallization process, i.e. crystallization temperature and crystallization-induced stress, of phosphorus-doped silicon thin films in order to eliminate crystal defects in single crystal substrates due to stress. Thus, the effect of phosphorus doping on the crystallization of films is discussed.

4. Effect of Phosphorus Doping on Crystallization

It is possible to observe the crystallization process of silicon thin films directly by using a scanning laser microscope⁽⁷⁾. However, the initial nucleation is not clear because of the 0.1- μm spatial resolution of the microscope. Thus, a transmission electron microscope was used to observe the initial nucleation process of the film in detail. A cross-sectional micrograph of an undoped film annealed at 630°C for 10 minutes is shown in Fig. 3. It is clear that the initial nucleation of silicon started at the interface of amorphous silicon and the base SiO_2 . In this figure, electron diffraction patterns obtained from the amorphous layer and nucleated particle are also shown. The nucleated particle was confirmed to be a single crystal. Similar results for initial nucleation from this interface were obtained from the observation of partially-crystallized phosphorus-doped silicon thin films.

However, it was found that the plane shape of the nucleated particle of the phosphorus-doped film is

Fig. 3 Cross-sectional transmission electron micrograph of a partially-crystallized silicon thin film

quite different from that of undoped films. Typical shapes of both films are shown in Figs. 4(a) and 4(b). Fig. 4(a) shows the nucleated particles of an undoped film. The particles are always oval and a single crystal. Electron diffraction analysis indicated that the (113) crystallographic plane of silicon mainly grew in films without doping. On the other hand, the nucleated particle of the phosphorus-doped films had a starfish-like shape as shown Fig. 4(b). Also, each particle was found to be not a single crystal but polycrystalline. Though each appendage of the particle grew as a single crystal in the (111) crystallographic plane of silicon, the longitudinal direction of each appendage was different, resulting in the polycrystalline phase of the starfish-like particle. In addition, energy dispersive X-ray analysis indicated that phosphorus concentration around the center of the particle was 30–50% higher than average dopant concentration. Thus, it can be assumed that the initial nucleation of the particle began at the highly-segregated phosphorus and this activated the crystallization proc-

Fig. 4(a) Plane transmission electron micrograph of a partially-crystallized silicon thin film without phosphorus doping

Fig. 4(b) Plane transmission electron micrograph of a partially-crystallized silicon thin film with phosphorus doping

ess of silicon. This segregation probably decreased the crystallization temperature of the phosphorus-doped silicon thin films.

Even if the doped phosphorus affected the crystallization process of silicon, the phosphorus existing at the interface of amorphous silicon and the base SiO_2 has the most important role. This is because nucleation always started at the interface. To confirm the effect of phosphorus on initial nucleation of the starfish-like particle, a very thin undoped layer about 5-nm-thick was deposited on the thermally-oxidized silicon wafer and then phosphorus doping at about $4 \times 10^{20}/\text{cm}^3$ to a thickness of about 550 nm was deposited on this undoped layer.

The change in the internal stress in this film during annealing is compared with that of film without an undoped layer in Fig. 5. The initial compressive stress of about 200 MPa in the amorphous film did not change. As reported above, crystallization started at about 580°C in the film without the undoped layer, while it started at about 620°C in the film with the undoped layer. This crystallization temperature agrees with that of film without phosphorus doping. Also, the crystallization-induced stress of film with the undoped layer increased to about 1200 MPa, 20% higher than that of the film without the undoped layer. The shrinkage rate of film with the undoped layer during crystallization also increased from 0.6% to 0.7%. This stress increase was found to be due to the increase in the average grain size of the crystallized film. It was about $2\text{ }\mu\text{m}$ in film without the undoped layer, while it increased to about $5\text{ }\mu\text{m}$ in film with the undoped layer. Since the increase in the average grain size decreases the volumetric ratio of the grain boundary, it causes an increase in stress because the grain boundary plays an important role in the stress relaxation process in the film.

Since initial nucleation started at the interface of

Fig. 5 Effect of the undoped layer in the phosphorus-doped silicon thin film on the change in the internal stress of the film

amorphous silicon and base SiO₂, the density of nucleated sites in film with the undoped layer is lower than that in film without the undoped layer where there is no segregation of phosphorus at the interface. This assumption of a lack of phosphorus segregation is supported by the fact that the crystallization temperature of the film with the undoped layer was almost the same as that of the film without doping. It is known that grain coarsening occurs in phosphorus-doped silicon thin films⁽¹⁰⁾. Thus, if the density of nucleated sites in the film with the undoped layer is low, the average grain size should be large.

Further, transmission electron micrographs showed that the shape of the plane of the nucleated particle in the film with the undoped layer was not starfish-like but oval, as observed in the film without doping. This structural change was also confirmed by X-ray diffraction analysis of fully-annealed films as shown in Figs. 6(a) and 6(b). Figure 6(a) shows the diffraction pattern obtained from film without the undoped layer. As it was observed by electron diffraction analysis, the (111) crystallographic plane of silicon grew mainly on this film. On the other hand, the (113) crystallographic plane grew mainly on the film with the undoped layer. This crystal growth pattern was the same as that of film without phosphorus doping.

These results clearly indicate that only the doped phosphorus existing at the interface of amorphous silicon and the base SiO₂ activates the crystallization

Fig. 6(a) X-ray diffraction pattern of the fully-crystallized film without doping

Fig. 6(b) X-ray diffraction pattern of the fully-crystallized film with phosphorus doping

process of silicon, i.e., lowers crystallization temperature. Even if the average dopant concentration is constant, the most important factor which dominates the crystallization process is the local concentration near the interface. Even the 5-nm undoped layer can change both the crystallization temperature of silicon thin films by about 40°C and crystallization-induced stress by about 20%. This result is very important from the viewpoint of stress control in semiconductor devices. Consequently, it is very important to keep the phosphorus concentration in amorphous silicon thin films near the interface of the base SiO₂ to maintain consistent quality when manufacturing phosphorus-doped silicon thin films.

The above-mentioned results were obtained from films deposited on thermally oxidized wafers, i.e., SiO₂. Thus, the base material has an effect on the crystallization process of phosphorus-doped silicon thin films. The doped films were deposited on a rinsed (001) single-crystal silicon wafer directly. The average phosphorus concentration was about $4 \times 10^{20}/\text{cm}^3$, and the undoped layer was not used.

Internal stress change of doped films deposited on the rinsed wafers is shown in Fig. 7. The initial compressive stress of the amorphous film was compressive stress of about 200 MPa, that is the same as the initial stress of the films deposited on SiO₂. This stress field did not change during annealing below 600°C. The crystallization temperature of the film deposited on Si was about 610°C, while that deposited on SiO₂ was 580°C. Besides, the crystallization-induced stress of the film deposited on Si increased from 1 000 MPa to 1 400 MPa. This stress increase corresponds to the increase in the average grain size from 2 μm to 7 μm. The nucleated particles were oval as shown in Fig. 8. Though this shape is the same as that observed in film without doping, or the phosphorus-doped film with the undoped layer, X-ray diffraction

Fig. 7 Effect of the base material on the change in the internal stress of the phosphorus-doped film

Fig. 8 Plane transmission electron micrograph of the partially crystallized film deposited on a rinsed silicon substrate

analysis showed that not the (113) but the (111) crystallographic plane of silicon grew mainly on this film. Thus, the crystallization process changed as a result of the change in the base material from SiO_2 to Si. Since the film was deposited on the (001) plane of silicon, it is concluded that epitaxial growth did not occur in the film. When a phosphorus-doped amorphous silicon thin film is deposited on the rinsed silicon surface, the doped phosphorus diffuses into the substrate silicon easily. Thus, there is no clear interface in this sample where the doped phosphorus can segregate. This interpretation is supported by the result that the crystallization temperature of film is close to that of the film without doping and doped film with an undoped layer. The lack of segregation of phosphorus therefore causes low density in the nucleation site of the film, and thus the large average grain size of nucleated particles.

The crystallization process and the crystallization-induced stress of phosphorus-doped silicon thin films are affected by the base material on which the film is deposited and the phosphorus concentration near the interface of the base and the film. Since it is very important to maintain consistent film quality in products in order to improve product reliability, further research is necessary to clarify the stress development mechanism and evaluate stress reduction methods.

5. Conclusions

The effect of phosphorus doping in amorphous silicon thin films on the crystallization process and the crystallization-induced stress of the film is discussed

experimentally. The initial residual stress of amorphous film was compressive at about 200 MPa, regardless of dopant concentration or base material. When the base material is SiO_2 , the crystallization temperature decreases with increase in dopant concentration. This is mainly due to the segregation of the doped phosphorus at the interface of the base and the film. The formation of a 5-nm thick undoped layer prevents segregation and thus, changes the crystallization process of the film. The crystallization-induced stress of the film depends on the base material and the phosphorus concentration at the interface of the film and the base. It varies from 1 000 MPa to 1 400 MPa. This stress change is mainly due to the increase in the average grain size of the crystallized film. The stress relaxation process at temperatures above 800°C also depends on the average phosphorus concentration. The higher the concentration, the lower the final residual stress of the fully annealed film. Therefore, it is very important to optimize film deposition and annealing conditions to maintain consistent film quality in products.

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