# FORMATION OF $Si_3N_4$ BURIED LAYERS IN SILICON UNDER THE ACTION OF HYDROSTATIC PRESSURE

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The methods of secondary-ion mass spectroscopy and transmission electron microscopy are used for the investigation of the influence of the hydrostatic pressure (HP) of nitrogen under high-temperature annealing on the synthesis of $Si_3N_4$ buried layers in silicon after the ion implantation of nitrogen. It is shown that the action of HP at a temperature of 1130°C stimulates the formation of a stoichiometric $Si_3N_4$ layer with abrupt phase interfaces and the high-level crystal perfection of surface layers of silicon. The creation of such structures can be related to the generation of interstitial defects and their influence on the formation of $Si_3N_4$ phase under the action of HP.

## 1. Introduction

Silicon-on-insulator (SOI) structures are widely used in the technologies of preparation of integrated circuits [1—3]. Despite a higher cost of SOI plates as compared to standard silicon ones, the price of ready devices prepared with the use of these plates can decrease due to the simplification of the technology and the decrease in the number of lithographic processes [4,5]. It's worth noting some other advantages of the SOI technology such as a higher radiation resistance of devices, increase in the integration level due to the absence of deep isolating regions, a high speed of operation of devices, and the essential decrease in the energy consumption.

The most developed technology of preparing the SOI structures is a high-dose implantation of $O^+$ ions into silicon with subsequent high-temperature annealing [4]. Among the defects of such a technology, one can indicate the necessity of a high implantation dose of oxygen ($4\times10^{17}$—$1.5\times10^{18}$ cm$^{-2}$), an essential (>1300 °C) annealing temperature required for the dissolution of $SiO_2$ precipitates in the upper Si layer, formation of a stoichiometric film of silicon oxide and also the appearance of considerable mechanical stresses that can result in the generation of defects in the process of thermal treatment. In many papers [6—8], the mechanisms of formation of dielectric layers in the process of implantation of nitrogen and nitrogen together with oxygen, which results in the creation of a buried layer of silicon nitride or oxynitride, were investigated. The implantation dose of nitrogen required for the formation of a $Si_3N_4$ stoichiometric layer is lower than that of oxygen required for the formation of a $SiO_2$ one. As the coefficients of thermal expansion of silicon nitride and dioxide deviate from that of silicon in different directions, it gives a possibility to decrease the magnitude of mechanical stresses by using oxynitride layers [6]. At the same time, there appears a number of problems associated with the crystallization of the nitride phase, which impairs the properties of both the dielectric layer and the silicon surface one. In the process of annealing, there takes place the accumulation of oxygen at Si—$Si_3N_4$ interfaces [8], which gives no possibility to create structures with abrupt interfaces. It's worth noting that the kinetics of the origin and the formation of a buried layer depends on both technological conditions and the concentration of point defects in the phase growth region. These effects can be used for stimulating the phase growth and obtaining the layers with abrupt interfaces [9—11].

Earlier, it was shown [12—14] that the thermal annealing of implanted silicon structures under the action of HP resulted in a number of specific effects, in particular, in a change of the kinetics of the formation of structural defects, thermal donors, etc. In the present paper, we have performed investigations of the formation of a buried $Si_3N_4$ layer in the process of thermal annealing under the action of hydrostatic compression as well as the redistribution of O and N impurities near the Si—$Si_3N_4$ phase interface.

## 2. Experiment

The *p*-type (100) silicon wafer (10 Ωcm) were implanted with $N_2^+$ ions with an energy of 140 keV and a dose of $1\times10^{17}$ cm$^{-2}$ at room temperature. A part of the samples (being control ones) was annealed at temperatures 800, 1000, and 1130 °C in nitrogen atmosphere. Another part of the samples was annealed at the same temperatures with the simultaneous action of HP 10.7 kbar in magnitude. After the annealing, we analyzed the profiles of the depth distribution of the elements (oxygen, nitrogen, and silicon) using the method of time-of-flight mass spectrometry. The sputtering of the surface of the investigated structures was fulfilled by cesium ions with an energy of 1 keV. In order to investigate the imperfection of the near-surface silicon layers and the properties of the Si—$Si_3N_4$ interfaces, the method of transmission electron microscopy was used.

## 3. Results

Figure 1 depicts the profiles of the impurities in the silicon structures implanted with nitrogen ions after high-temperature annealing performed under various conditions. In the structures annealed at a temperature of 800 °C (Fig. 1,*a*), the profile of nitrogen is close to that calculated theoretically with a maximum of the distribution located at a depth of about 180 nm. The presence of nitrogen HP in the process of annealing doesn't influence the form of the impurity distribution. One can also observe a slight increase of the oxygen concentration in the region of the maximum of the nitrogen distribution.

The annealing performed at a temperature of 1000 °C (Fig. 1, *b*) results in the formation of complicated profiles of the nitrogen distribution. Nitrogen is accumulated in a surface Si layer with a maximum at a depth of 60—80 nm from the surface and at a depth of 150—250 nm. In the region of the maximum concentration of nitrogen, one can observe the accumulation of oxygen

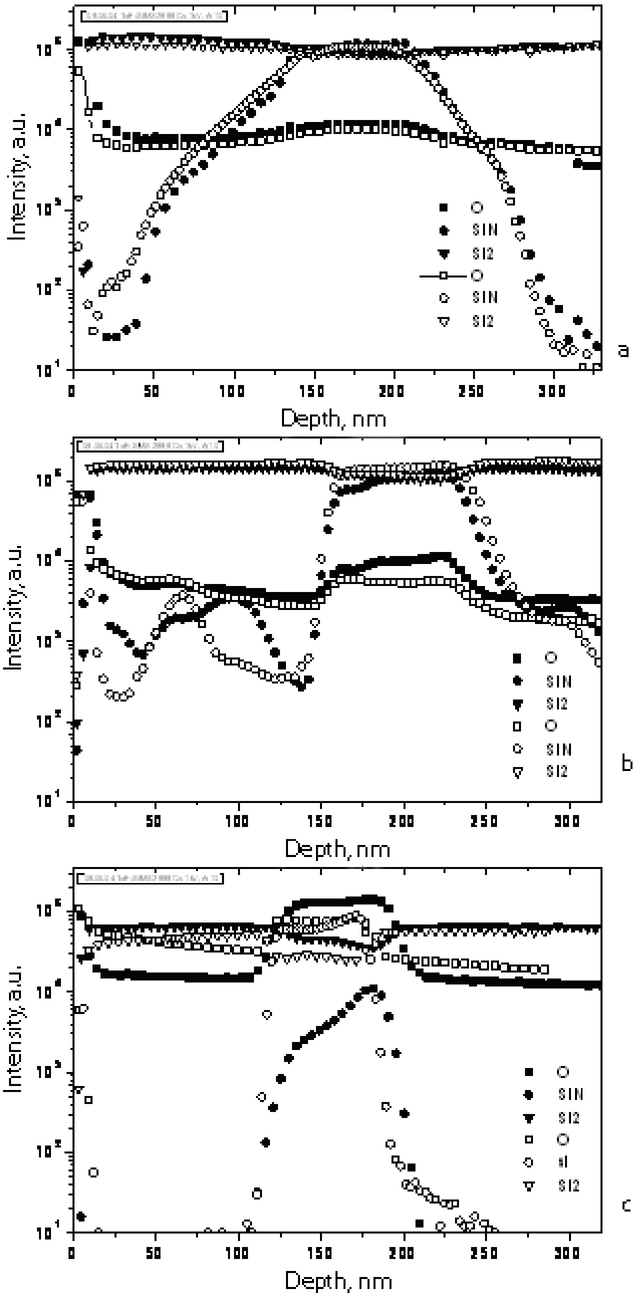
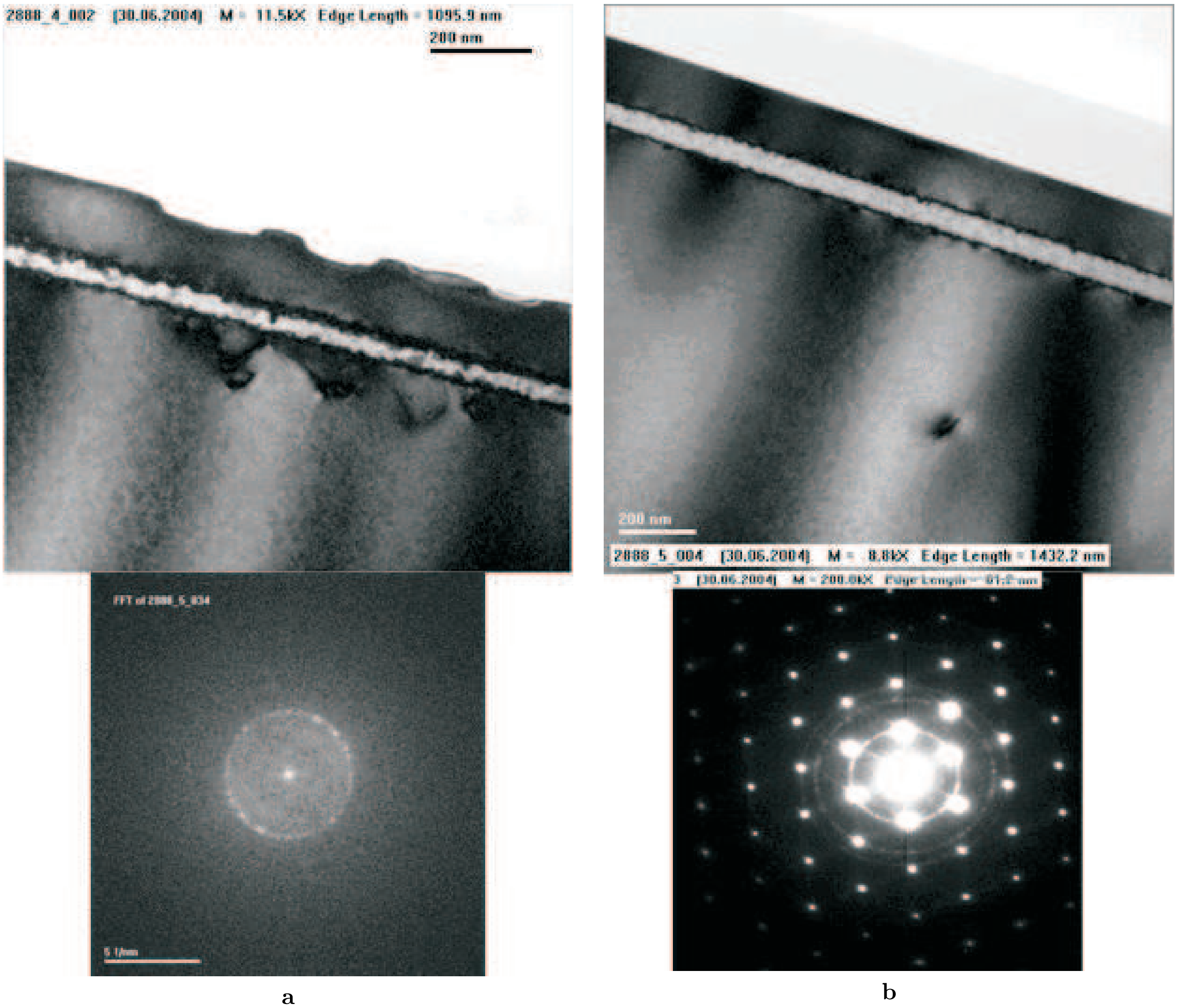


Fig. 1. Distribution profiles of impurities in Si implanted with nitrogen ions after thermal annealing: *a* — 800 °C, *b* — 1000, *c* — 1130 (■ • ▼ — without HP, □ ○ ∇ — under the action of HP)



**a** **b**

Fig. 2. Electron-microscopic images of the cross sections and the electron diffraction patterns of Si samples implanted with nitrogen ions and annealed at $T$=1130 °C without ($a$) and under the action of ($b$) HP

with a distribution of approximately rectangular form. The action of HP gives rise to the following effects: a decrease of the nitrogen concentration on the surface and in the surface Si layer, a decrease of the oxygen concentration, and a slight increase of the nitrogen concentration in the region, where the buried $\mathrm{Si}_x\mathrm{N}_y$ layer is formed. The relation between the signals from $\mathrm{Si}_2$ and SiN from depths of 150—230 nm indicate to the fact that the nitride phase doesn't correspond to the stoichiometric phase of $\mathrm{Si}_3\mathrm{N}_4$.

In Fig. 1,$c$, we present the profiles of the impurities in the structures annealed at a temperature of 1130 °C. In the samples annealed without the action of HP, nitrogen is distributed at depths of 100—220 nm. Its concentration in the maximum of the distribution is much lower than that reached at low-temperature annealing. At the same depth, there takes place the accumulation of oxygen. In the structures annealed under the action of HP, a stoichiometric $\mathrm{Si}_3\mathrm{N}_4$ layer with abrupt phase interfaces is formed at a depth of 110—200 nm, and the accumulation of oxygen is insufficient.

Figure 2 shows the electron-microscopic images of the cross sections of the samples annealed at $T$=1130 °C under the action of HP and without it, as well as the electron diffraction patterns of the surface crystalline layer of silicon. One can see that, without the action of HP, the buried layer is inhomogeneous and includes a high concentration of defects at the phase interfaces. One can also observe defects on the surface of the sample. The image of the electron diffraction patterns indicate to the presence of microcrystalline inclusions in the surface Si layer. In the samples annealed under pressure, we observed a buried layer of 65 nm in thickness with abrupt interfaces. The electron diffraction patterns indicate a high level of crystallinity of the surface layer of silicon.

## 4. Discussion of the Results

At low annealing temperatures, the formation of SiN bonds and precipitates of the nitride phase takes place in the regions of the maximum concentration of nitrogen atoms. At such temperatures, the diffusion of atoms is insufficient, $Si_xN_y$ precipitates don't decay, no continuous buried layer is formed, and the surface layer represents a mixture of Si microcrystals and $Si_xN_y$ precipitates.

With increase in the annealing temperature, a considerable part of nitrogen diffuses onto the sample surface. A buried nonstoichiometric $Si_3N_4$ layer is also formed. As the formation of the $Si_3N_4$ phase requires interstitial Si defects, a buried layer is formed at the depth $R_p + \Delta R_p$, where an excess of interstitial defects is present. A free volume in the phase growth region causes the gettering of oxygen to this zone. Under the action of HP, additional interstitial defects are formed, which retards the diffusion of nitrogen to the surface and promote to the creation of the $Si_3N_4$ phase. However at $T$=1000 °C, the amount of the generated interstitial defects is insufficient, and the phase is formed in the same region as that in the control sample. Additional interstitial atoms that arise under hydrostatic compression decrease the effect of the gettering of oxygen.

With increase in the annealing temperature in the control samples, an essential part of nitrogen is lost due to the diffusion into the environment. At this temperature, SiN surface bonds decay, that's why one cannot see N atoms on the surface.

There takes place the gettering of oxygen from both the surface and the volume of the sample to the regions of the formation of the $Si_3N_4$ phase, which results in the formation of a silicon oxynitride phase in this zone.

The presence of HP at such a temperature gives rise to the additional generation of interstitial defects, whose number is much higher than that of residual post-implantation defects. This results in the formation of the $Si_3N_4$ stoichiometric phase in the region of the maximum of the nitrogen distribution. The additionally generated interstitial defects diffuse to the growth region of the $Si_3N_4$ phase, where a free volume exists, which stimulates a further growth of the phase. Under the action of HP, the $Si_3N_4$ surface film is also stable, whereas it decays at this temperature in the control sample.

Thus, at high temperatures, the action of HP allows one to control the process of synthesis of $Si_3N_4$ buried layers, to stimulate the formation of a stoichiometric film near the maximum of the distribution of implanted nitrogen, and to essentially decrease the smearing of the phase interfaces at the expense of the additional injection of interstitial defects.

## 5. Conclusions

The nucleation and growth of a $Si_3N_4$ buried layer at $T$=1000 °C in nitrogen-implanted Si substrates is accompanied with the gettering of oxygen into the region of the phase growth. The influence of HP on the investigated structures decreases this effect due to the injection of interstitial defects.

The increase of the annealing temperature to 1130 °C essentially changes the conditions of synthesis of the $Si_3N_4$ phase. In the control samples, an inhomogeneous oxynitride film at depths $R_p - \Delta R_p$ is formed. The action of HP stimulates the formation of a stoichiometric buried $Si_3N_4$ film with abrupt phase interfaces Si—$Si_3N_4$—Si near the maximum of the concentration of implanted nitrogen. A high crystal perfection of the surface film is discovered. The mechanism of the action of hydrostatic compression is associated with the generation of interstitial defects and their influence on the creation and growth of the $Si_3N_4$ film.

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# ФОРМУВАННЯ ПРИХОВАНИХ ШАРІВ $Si_3N_4$ В КРЕМНІЇ ПІД ДІЄЮ ГІДРОСТАТИЧНОГО ТИСКУ

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Резюме

Методами вторинної іонної мас-спектрометрії та просвічуючої електронної мікроскопії досліджено вплив гідростатичного тиску (ГТ) азоту при високотемпературних відпалах на синтез прихованих шарів $Si_3N_4$ в кремнії після іонної імплантації азоту. Показано, що дія ГТ при температурі 1130°C стимулює формування стехіометричного шару $Si_3N_4$ з різкими межами поділу фаз та високим рівнем кристалічної досконалості приповерхневих шарів кремнію. Утворення таких структур можна пов'язати з генерацією міжвузловинних дефектів і їхнім впливом на формування фази $Si_3N_4$ під дією ГТ.