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# Improving stress stability in low-pressure chemical vapor deposited silicon dioxide films by ion implantation

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A B S T R A C T

The stress state of low-pressure chemical vapor deposition (LPCVD) silicon dioxide ($SiO_2$) films fluctuates upon aging due to the ambient moisture. The related variation of the $SiO_2$ films is a key factor of device reliability. In this study, ion implantation is introduced to improve film stress stability. The stress state modified by ion implantation is discussed in detail and an analytical model is presented. The evolution of the stress in as-deposited and $P^+$-, $As^+$-, and $B^+$-implanted LPCVD $SiO_2$ films upon aging is investigated, and the bonding nature of the films is also studied to provide insight into the physical mechanisms involved. It is demonstrated that low implantation energy slightly modifies the stress in films. In addition, $P^+$ ion is the most appropriate impurity ion to improve film stress stability, and the stress in $P^+$-implanted LPCVD $SiO_2$ film can be stabilized with a low tensile stress of 67 MPa when the film is implanted at 15 keV with a dose of $1 \times 10^{15}$ $cm^{-2}$.

## 1. Introduction

Low-pressure chemical vapor deposition (LPCVD) is a basic thin film deposition technology. Silicon dioxide ($SiO_2$) films grown by LPCVD are widely used in integrated circuits (ICs) and microelectromechanical systems (MEMS). They are commonly employed as the passivation layer, mask layer or sacrificial layer [1–3]. Due to their good mechanical and insulating properties, LPCVD $SiO_2$ films can also be used as the structural layer of MEMS devices, such as the membrane of vibrating resonators [4], the dielectric of micro-scanning mirrors [5], and the cantilever of infrared (IR) imaging detectors [6].

Stress is inherent in LPCVD $SiO_2$ films due to deposition processes, and it has a significant influence on the performance of devices. Stress in LPCVD $SiO_2$ films is known to be prone to drift with time in the ambient atmosphere, which would cause structural deformation and functional degradation [7]. This is an important issue related to the device reliability. A lot of researchers have studied the stress evolution of $SiO_2$ stored in the ambient atmosphere. Haque and Guan *et al.* showed that the stress continues to decrease progressively with increasing aging time [8,9]. Park *et al.* pointed out that the evolution of stress is due to both structural changes in Si—O network and water molecules absorbed on walls of the pores [10]. Bakos *et al.* reported that the most stable form of water in $SiO_2$ is the interstitial molecule, and vicinal silanol groups may form at a low-energy cost with a barrier of 1.5 eV [11].

The mechanism of stress evolution in $SiO_2$ has been gradually understood. However, there is still lack of an effective way to stabilize the film stress in the ambient atmosphere. In this work, ion implantation is used to stabilize the stress in LPCVD $SiO_2$ films. Ion implantation is an attractive method since the implantation dose and energy can be accurately controlled and the implanted ions can precisely affect the Si—O network. The stress state of LPCVD $SiO_2$ films implanted at different energies is studied, and an analytical model is developed to describe the stress modification. Then the effects of implantation ion types and doses on the stress evolution upon aging are systematically investigated, and a physical mechanism is proposed and discussed.

## 2. Experiments

### 2.1. Sample preparation

The experimental procedure starts with 4-in. silicon wafers. 300 nm-thick $SiO_2$ films are prepared by a Thermco LPCVD furnace using tetraethylorthosilicate (TEOS) as the source material. The deposition temperature is 730 °C, and the total deposition pressure is 0.5 Torr. The back-side $SiO_2$ films are removed by buffered oxide etch (BOE), while the front-side films are protected by MEGAPOSIT S9920 photoresist. Next, the photoresist is removed by acetone, and the front-side $SiO_2$

**Table 1**
Process parameters for ion implantation.

| Implanted impurity | Energy (keV) | Dose ($cm^{-2}$) |
|---|---|---|
| P | 15 | $5 \times 10^{13}$, $1 \times 10^{14}$, $5 \times 10^{14}$, $1 \times 10^{15}$ |
| | 30, 60 | $1 \times 10^{15}$ |
| As | 35 | $1 \times 10^{15}$, $3 \times 10^{15}$ |
| $BF_2$ | 23 | $1 \times 10^{15}$, $3 \times 10^{15}$ |

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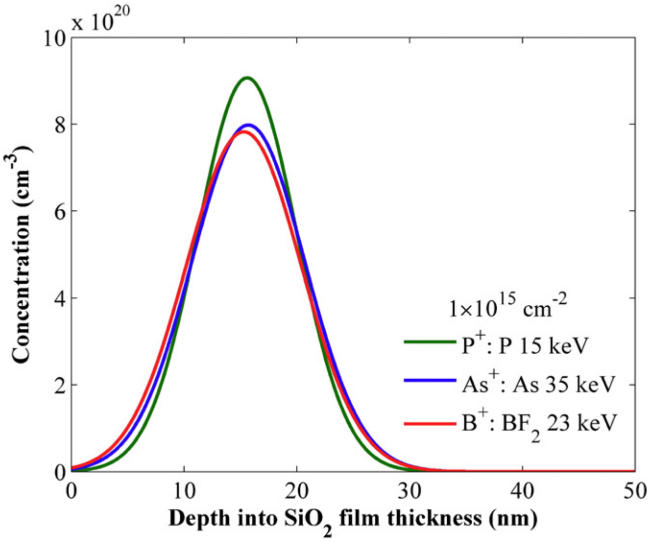

**Fig. 1.** Calculated distribution of ions in $SiO_2$.

**Table 2**
Film stress measured after the second annealing treatment.

| Films | Projected range (nm) | Measured stress (MPa) |
|---|---|---|
| As-deposited | 0 | 70 |
| Implanted with P at 15 keV | 15.6 | 67 |
| Implanted with As at 35 keV | 15.7 | 67 |
| Implanted with $BF_2$ at 23 keV | 15.3 | 68 |
| Implanted with P at 30 keV | 31.2 | 42 |
| Implanted with P at 60 keV | 62.5 | 17 |

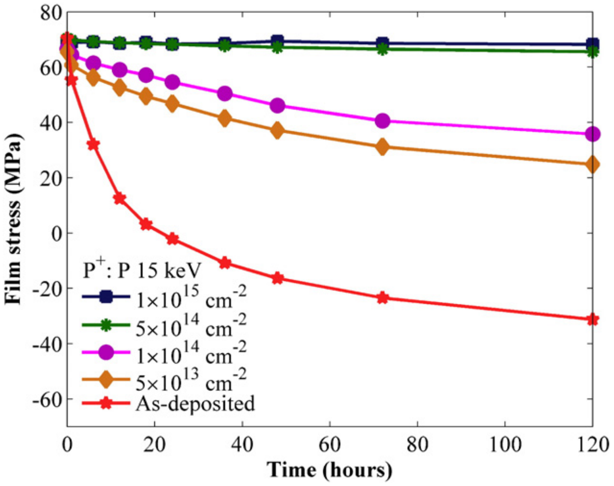

**Fig. 3.** Film stress as a function of aging time for as-deposited and $P^+$-implanted $SiO_2$ films.

films are rinsed by de-ionized water. Annealing at 800 °C for 120 min in a nitrogen ($N_2$) filled furnace is then taken to make the front-side $SiO_2$ film densification.

After that, one sample is used as a reference, and others are separately implanted with phosphorus (P), arsenic (As) or boron difluoride ($BF_2$) by a ULVAC IM-200 M implanter. P, As and $BF_2$ are chosen because they are commonly used as impurities in ICs and MEMS. $BF_2$ is used instead of boron (B) for ultra-shallow $B^+$ ion implantation, $B^+$ and $F^+$ ions are dissociated in the process of implantation, and $F^+$ ion out-diffuses and leaves the films after annealing [12]. Experiments of implantation are carried out by varying the implantation energies and doses (see Table 1). The different implantation energies of 15 keV, 35 keV and 23 keV are chosen for the same projected range (about 15 nm), so the similar implanted profiles can be obtained at the same dose according to Gaussian distribution function [13], as shown in Fig. 1. For $P^+$ ion implantation, implantation energies of 30 keV and 60 keV are also investigated, while the implantation dose is set to be $1 \times 10^{15}$ $cm^{-2}$.

All films are annealed by furnace at 800 °C for 120 min in dry $N_2$ ambience to recover most damages. Then the films are stored in a class 100 cleanroom environment with a relative humidity (RH) of 45%.

### *2.2. Sample measurements*

Film thickness is measured using a Nanometrics NanoSpec AFT 4000 by analyzing the interference spectra when light passes through the film. Film stress is measured with the wafer curvature measurement

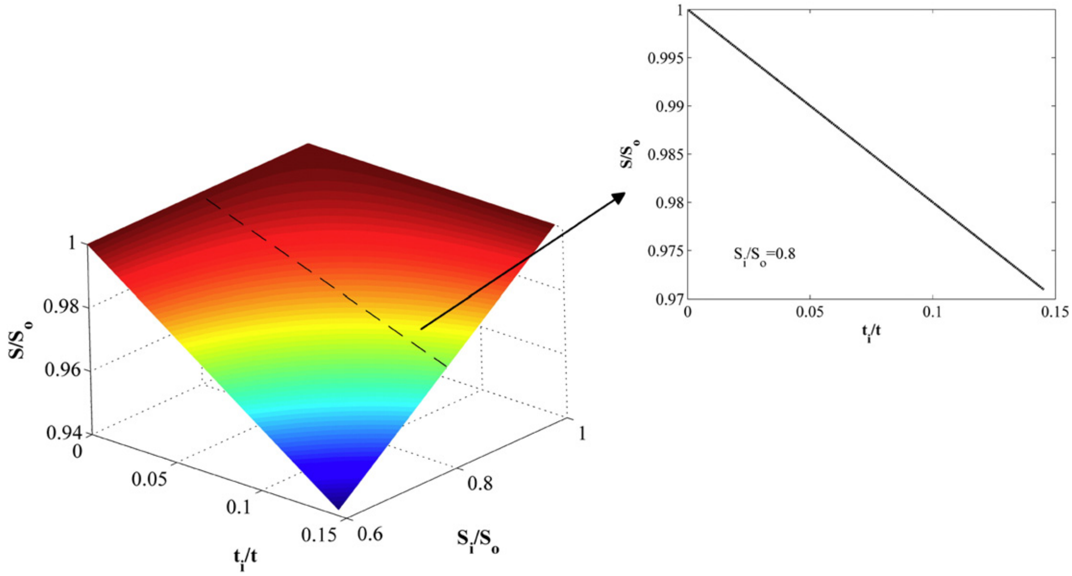

**Fig. 2.** Theoretical analysis of the film stress, as a function of properties of the thickness ratio of implanted layer to $SiO_2$ film and the stress ratio of implanted layer to bare layer.