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# High Reliability Poly-Oxide Grown on in-situ Phosphorus Doped Amorphous Si

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A high reliability poly-oxide was obtained by oxidizing *in-situ* phosphorus doped amorphous silicon. Critical electric field, $E_c$, of the poly-oxide increased with dopant concentration, and reached 7.5MV/cm, which is comparable to the oxide of single crystalline Si. $E_c$ showed no decrease for Si films that contained as much as $2\times10^{21}$ $cm^{-3}$ dopants. Conventional models cannot explain the high $E_c$. We proposed a new model in which defect reduction in grains lead to the high $E_c$ on the highly-doped Si film.

## INTRODUCTION

Thermal oxide on deposited silicon films(poly-oxide) is widely used as interpoly dielectrics in nonvolatile memories such as EPROMs and EEPROMs1). Applicable electric field of the conventional poly-oxide is rather small compared to $SiO_2$ on single crystalline Si. This has been attributed to (1)the locally enhanced electric field that is a result of the rough $SiO_2$/poly-Si interface2) and/or (2)the phosphorus intrusion into the $SiO_2$3). This degradation is an obstacle to increasing the integrity of nonvolatile memories.

Previously, we reported a novel poly-Si which was deposited in an amorphous state with *in-situ* phosphorus doped. This film has large grains with 1-2μm long4). In addition, it has a flat surface. These properties are expected to improve the poly-oxide reliability, which is reported in the following.

## EXPERIMENTAL

### 1. Sample Preparation

MOS capacitors(Fig.1) were fabricated for measuring current-voltage(I-V) characteristics of the poly-oxide. Here, two types of lower poly-Si electrodes were formed utilizing LPCVD. One type was the conventional poly-Si which was deposited at 625°C using $SiH_4$. This Si film was covered by 10nm-thick $SiO_2$ film deposited at 800°C, and then doped with phosphorus by ion implantation at 40keV. The CVD $SiO_2$ was removed after the implantation. The other type of electrode

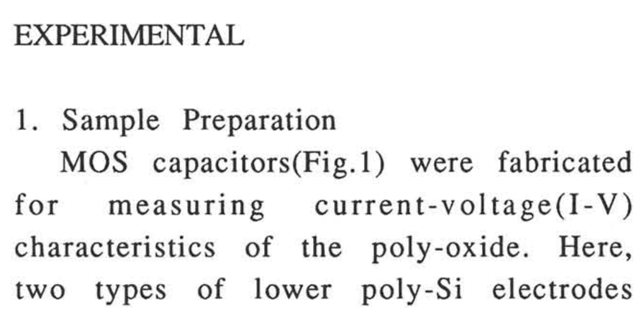

Fig.1 MOS capacitor for measuring I-V of poly-oxide

was *in-situ* doped amorphous Si film deposited at 525°C using $Si_2H_6$ and $PH_3$. Phosphorus concentration in the film was varied by controlling the $PH_3$ flow rate. After patterning the Si films, 20nm-thick poly-oxide was formed at 1000°C in 10% $O_2$(diluted by Ar). Then, upper electrodes (gates) were formed by patterning *in-situ* doped a-Si films containing $3.7\times10^{20}cm^{-3}$ phosphorus. Annealing at 650°C completed the sample preparation.

2. Measurements

Dopant and carrier concentration in the films were measured by fluorescence X-ray analysis(FXA), and Hall effect measurement using the van der Pauw method$^{5)}$.

I-V curves were measured by applying a step voltage to the gate. Capacitor area ranged $0.5\text{-}1.9mm^2$.

Crystallinity of the Si films after oxidation was observed by a transmission electron microscope(TEM).

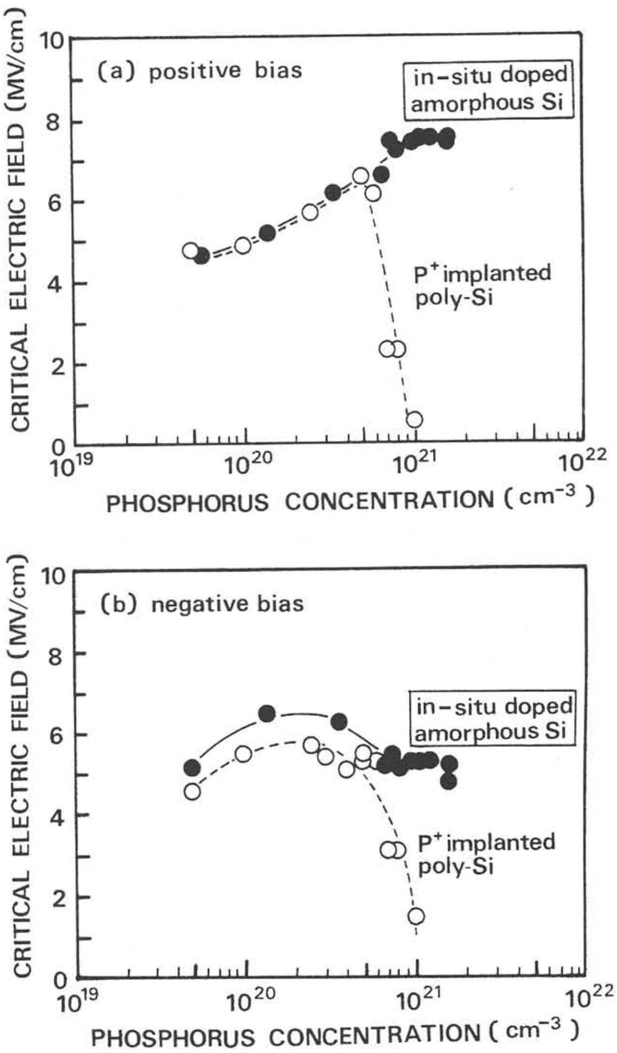

Fig.2 Critical electric field vs phosphorus concentration in lower poly-Si electrodes when (a)positive and (b)negative bias was applied upper poly-Si electrodes

RESULTS

Critical electric fields, $E_c$, of the poly-oxide are shown in Fig.2 as a function of the phosphorus concentration in the lower poly-Si electrodes. $E_c$ is that field which induces a leakage current of $1\mu A/cm^2$. First, we investigated the case of the positive bias (Fig.2(a)). The $E_c$ for the conventional implanted poly-Si increased with the dopant concentration less than $5\times10^{20}cm^{-3}$, and abruptly decreased at higher concentration. By contrast, the $E_c$ for the *in-situ* doped a-Si increased continuously, and showed no decrease in the range of P concentration investigated. The maximum $E_c$(7.5MV/cm) is comparable to the value 8MV/cm in $SiO_2$ on single crystalline Si. Similar results were obtained for the negative bias (Fig2(b)).

DISCUSSION

Next we discuss the mechanism of the high $E_c$ for *in-situ* doped a-Si.

1. Dopant Intrusion

It has long been suspected that the dopant intrusion into the oxide degrades

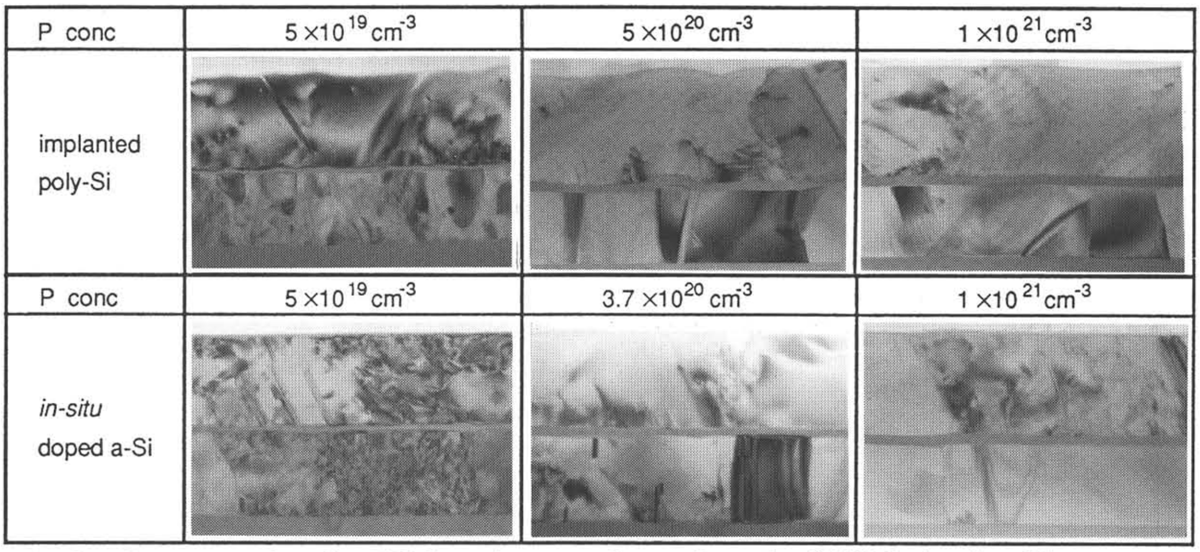

Fig.3 Cross-sectional TEM micrographs of poly-Si/$SiO_2$/poly-Si structures

the poly-oxide[3]. However, this effect does not seem important here, because a high $E_c$ is obtained for the *in-situ* doped a-Si with as much as $2\times10^{21}cm^{-3}$ phosphorus.

### 2. Asperity of $SiO_2$/Si Interface

The asperity of the interface is shown in Fig.3. In the implanted poly-Si, the flatness of the interface improved with the dopant concentration. On the other hand, the interface was extremely flat, independently of the P concentration, in the *in-situ* doped a-Si films. These results indicate that the asperity of the interface does not affect the $E_c$.

### 3. Defects in the poly-Si Grains

It is noteworthy in Fig.3 that there exist more defects in the grains of the *in-situ* doped Si films with a lower dopant concentration even though the grain sizes are almost the same. The defects are also reflected in the Si film property itself. Figure 4 shows the relationship between the carrier concentration and the mobility of the *in-situ* doped a-Si films. The films are polycrystalline after annealing. For the carrier concentration below $1\times10^{20}cm^{-3}$, the mobility increased with the carrier concentration and the annealing temperature. Because the grain size is independent of phosphorus concentration[4], this change may be attributed to defect density reduction in the grains. The defect density should be more reduced above $1\times10^{20}cm^{-3}$ carriers, though the mobility decreased because of the Coulomb scattering.

These defects seem to degrade the

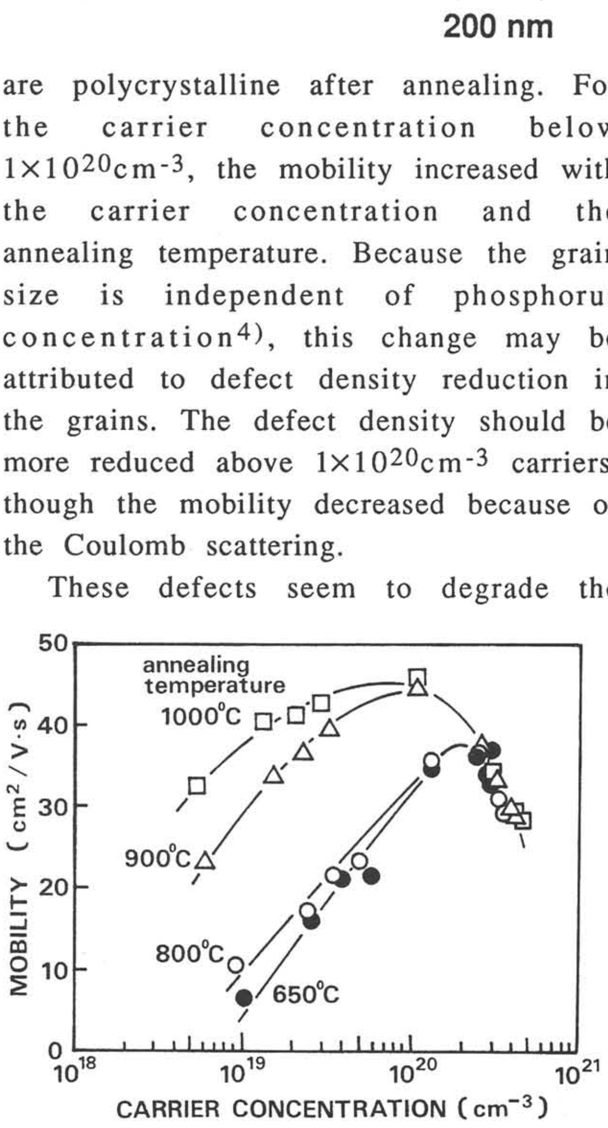

Fig.4 Carrier concentration vs mobility of *in-situ* doped Si films

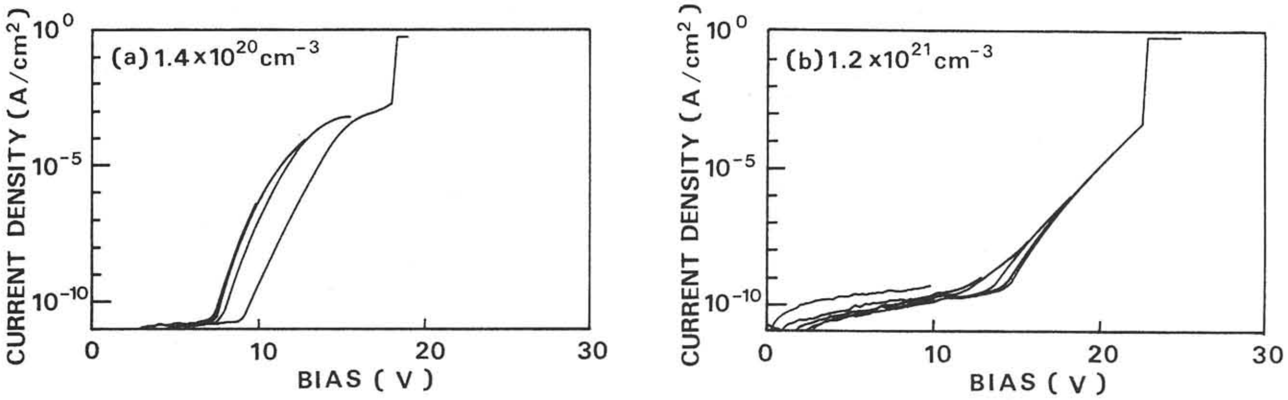

Fig.5 I-V characteistics of poly-oxide grown on *in-situ* doped a-Si containing (a)$1.4\times10^{20}$cm$^{-3}$ and (b) $1.2\times10^{21}$cm$^{-3}$ phosphorus when positive bias was repeatedly applied and released

poly-oxide quality. The degradation was investigated from the view point of carrier traps in the following. Figure 5 shows the I-V characteristics of the poly-oxide on the *in-situ* doped a-Si where a positive bias was repeatedly applied and released. When phosphorus concentration in the lower Si film was $1.4\times10^{20}$cm$^{-3}$, the current decreased after each application of the bias(Fig.5(a)). This was not remarkable when the lower Si film contained $1.2\times10^{21}$cm$^{-3}$ phosphorus (Fig5.(b)). These decreases in the current are usually observed in $SiO_2$ on single crystalline Si when the $SiO_2$ contains carrier traps$^{6)}$. These results suggest that there are more carrier traps in the poly-oxide on the less doped Si film. The traps seem to be produced by the defects in the grains. Thus, we consider that the continuous increase in the $E_c$ with the P concentration results from the defect reduction in the grains.

## CONCLUSION

A high reliability poly-oxide was obtained by oxidizing *in-situ* doped amorphous Si film. The critical electric field of the oxide increased with the dopant concentration, reaching 7.5MV/cm, which is comparable to the oxide on single crystalline Si. This seems to result from the reduction of the defects in the highly-doped Si grains. This poly-oxide will be the key to realizing high-integrity EEPROMs.

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