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OXYGEN RELATED TRANSPORT PHENOMENA NEAR THE POLYSILICON/SiO₂ INTERFACE ON SILICON DURING PHOSPHORUS DIFFUSION

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The structural modifications near the polysilicon/SiO₂ interface on Cz silicon substrate during the phosphorus diffusion from a liquid POCl₃ source were investigated by cross-silicon transmission electron microscopy (XTEM). A thick (1.5 μ) polysilicon layer was deposited by the LPCVD method at 620°C and a phosphorus prediffusion at 1030°C for 15 min and a diffusion at the same temperature for 20 min were subsequently performed. The SiO₂ precipitation process from the dioxide layer of 16 nm thickness was discussed taking into account both the oxygen atom transport from the SiO₂ interfacial layer and from silicon bulk of the substrate, in interaction with the silicon self-interstitial atoms generated by the phosphorus diffusion in silicon and by the polysilicon oxidation during the phosphorus prediffusion.

1. INTRODUCTION

Recently it was described the influence of the phosphorus doping on the restructuring process of the polysilicon layers on silicon during phosphorus diffusion in the polysilicon/silicon system from a POCl₃ liquid source [1]. Such a system is useful because it improves the electrical parameters of the npn transistors and their reliability, as well as for microsystem applications [2]. It was shown [1] that the phosphorus diffusion influences the restructuring process of the polysilicon layers, determining the enhancement of the grain growth due to the silicon self-interstitial injection induced by phosphorus diffusion in the silicon grain bulk and in the silicon substrate. During the phosphorus diffusion from the liquid POCl₃ source, self-interstitial atoms are generated by the oxidation

process associated to the phosphosilicate (PSG) growth on the top of the polysilicon layer. Restructuring process also influences the doping properties, especially near the polysilicon/SiO₂ interface on silicon [2].

In this paper we discuss new results concerning the behaviour of the polysilicon/SiO₂/silicon system during the phosphorus diffusion from a POCl₃ source (prediffusion step) and during the subsequent diffusion treatments, especially consisting in the degradation of the thick (16nm) interfacial layer and SiO₂ precipitation in the silicon substrate near the polysilicon/SiO₂ interface. A mechanism of this precipitation is proposed. Such a mechanism involves the oxygen transport from the initial continuous SiO₂ film to the silicon region near the polysilicon/SiO₂ interface and determines the extension of the SiO₂ precipitated film to the silicon bulk. The influence of the oxygen atoms from Cz type silicon wafers on the SiO₂ precipitation near the polysilicon/SiO₂ interface is also discussed. New mechanisms of atomic transport are pointed out, explaining the enhancement of the SiO₂ precipitation process and then the extension to the silicon bulk of the SiO₂ precipitation region.

2. EXPERIMENTAL CONDITIONS

A polysilicon layer with thickness of about 1500 nm was grown by low pressure chemical vapour deposition (LPCVD) at the pressure of 0.2 torr and the temperature of 620°C on p-type, (111)-oriented, Cz silicon wafers with a resistivity of (8–12) Ωcm. The polysilicon layer was phosphorus doped by diffusion from a liquid POCl₃ source at the temperature of 1030°C for 15 min. After the phosphorus prediffusion, the polysilicon heat treatment was continued by a subsequent annealing for 20 min at the same temperature of 1030°C to drive-in the dopant by a diffusion process into the silicon.

Three types of samples were investigated: specimen 1 with the polysilicon layer as deposited, specimen 2 after phosphorus prediffusion from POCl₃ source at 1030°C for 15 min and specimen 3 after drive-in diffusion by annealing at 1030°C for 20 min. After each step of annealing there were determined the junction depths in silicon to observe the doping conditions of the thick-polysilicon system. The junction depth of the specimen 2 and 3 were determined by cross-sectional electron-beam induced current (EBIC) measurements with a JSM 840 scanning electron microscope.

In order to correlate the structural modifications of the polysilicon layer with the phosphorus diffusion conditions, the specimens of type 1, 2 and 3 were also examined by a JEM 2000 FX transmission electron microscope (TEM) to delineate the structural morphology of the polysilicon and polysilicon/silicon interface.

3 RESULTS

The main results obtained from TEM determinations are shown in Figs. 1-3. Fig. 1 shows a TEM cross-sectional micrograph of the thick polysilicon/silicon

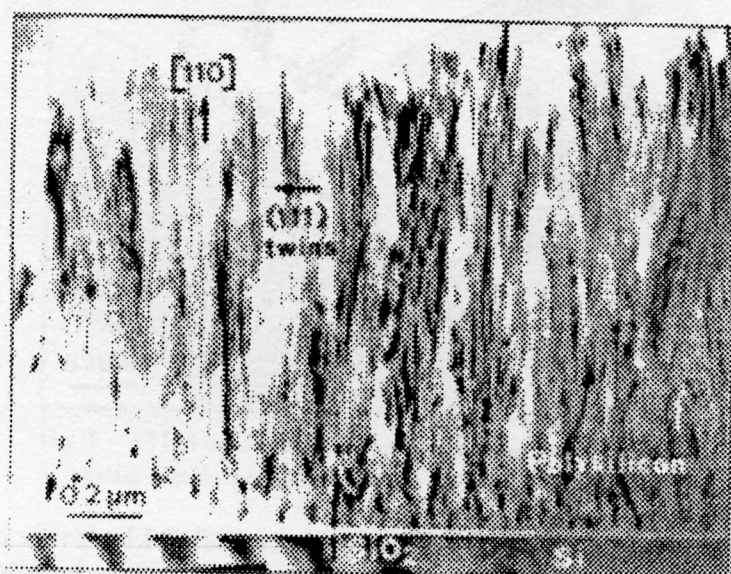


Fig. 1 - XTEM cross-sectional micrograph of the polysilicon/SiO₂/silicon system after the LPCVD process at 620°C.

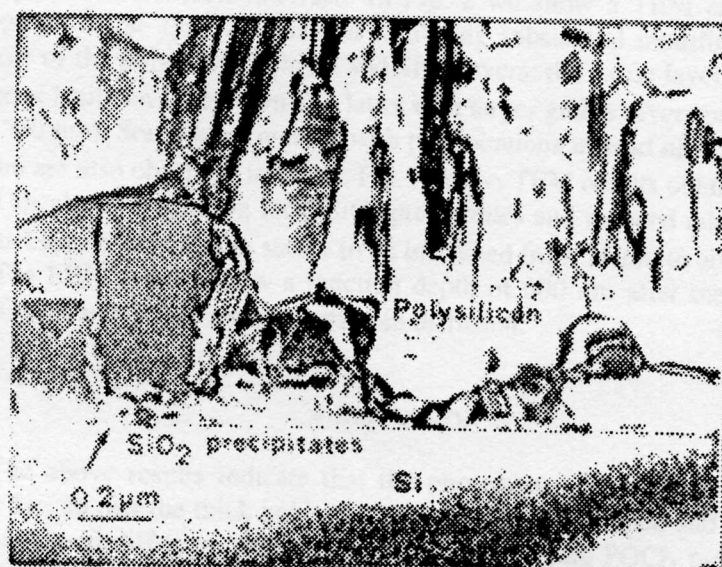


Fig. 2 - XTEM cross-sectional micrograph of the polysilicon/SiO₂/silicon system after the phosphorus prediffusion at 1030°C for 15 min.

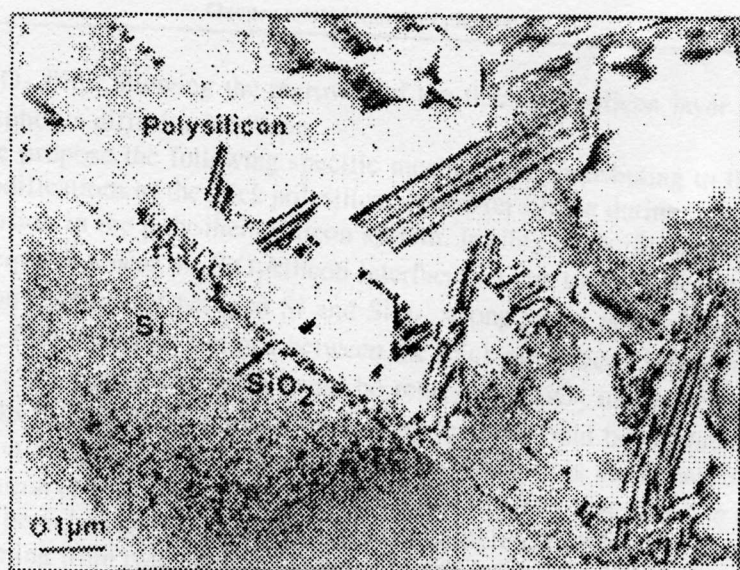


Fig. 3 - XTEM cross-sectional micrograph of the polysilicon/SiO₂/Si system after the phosphorus drive-in diffusion at 1030°C for 20 min.

system after the LPCVD process. A columnar structure of [110] oriented grains are observed within the deposited thick polysilicon layer, characterising its initial morphology. A continuous SiO₂ film of thickness of about 16 nm is present at the polysilicon/silicon interface. In Fig. 2 we show a TEM cross-sectional micrograph of the type 2 specimen exhibiting substantial modifications in the structure of the polysilicon/silicon and SiO₂ layers: the oxide layer is broken up and the polysilicon is regrown to a layer with larger grains (average grain size of about 300 nm). Some local regions with precipitations instead of a SiO₂ continuous film are also observed in Fig. 2. Fig. 3 shows TEM results obtained from the type 3 specimen exhibiting local SiO₂ precipitates and isolated islands of SiO₂. The thickness of this region seems to be increased from 16 nm to about 20 nm.

The EBIC results show a junction depth of 600 nm after the phosphorus prediffusion and of 800 nm after drive-in diffusion.

4. DISCUSSION

The above results indicate that the phosphorus doping process is sufficiently fast so that the thick polysilicon layer to be fully doped and therefore to become a local diffusion source for silicon after 15 min POCl₃ prediffusion at 1030°C. Such a result shows that the moderate temperature (1030°C) short-time duration (15 min) phosphorus diffusion annealing is sufficient to break-up the

thick SiO_2 film, allowing the regrowth of the thick polysilicon layer and then the phosphorus diffusion in silicon.

We propose the following specific mechanisms contributing to the structural modifications of the thick polysilicon layers on silicon during the phosphorus diffusion in the polysilicon/silicon system, leading to the SiO_2 breaking-up and precipitation near the SiO_2 /silicon interface: (i) due to the different thermal expansion coefficients between Si and SiO_2 , strong stress is developed within the SiO_2 film which is confined between the thick-polysilicon layer and the Si substrate; the high strain fields could be relaxed by SiO_2 mechanical damage like cracks in local weak regions; such weak regions could be created by local conversion of SiO_2 into phosphosilicate glass (PSG) as a consequence of the incorporation of high phosphorus concentration ($>1\%$) by fast diffusion through the grain boundaries; (ii) the silicon self-interstitial injection into the polysilicon layer, coming from two sources: (1) the oxidation of the polysilicon surface and the conversion into the phosphosilicate glass, in the ambient of POCl_3 , O_2 and N_2 gases during the phosphorus prediffusion; (2) the phosphorus diffusion itself, contributing to an efficient and short-time regrowth into a larger grain size structure, induces a rapid SiO_2 degradation as we will present below.

As the first type of mechanism is concerned, we have to take into account that the excess phosphorus atoms diffusing from the surface along the columnar grain boundaries should be effective especially during the first stages of the prediffusion, when the density of the fast diffusion paths is sufficiently high and short. Therefore, according to the proposed mechanism (i), we have to expect an efficient process of breaking-up of the SiO_2 layer during the phosphorus prediffusion (Fig. 2).

The SiO_2 precipitation observed from Fig. 2 and Fig. 3 can be explained by the silicon self-interstitial participation at the local atomic transport. Due to the excess of silicon self-interstitial atoms coming from the phosphorus diffusion and from PSG growth process, a simple reaction including SiO_2 decomposition occurs as:



SiO is a mobile species [5] with a diffusion coefficient in the SiO_2 layer of the order of $10^{-15} \text{ cm}^2/\text{s}$ at 1030°C . This species can diffuse away from the polysilicon/ SiO_2 interface and precipitate by the reverse reaction, or can be lost by diffusion along the grain boundaries (Fig. 3). Such a process determines the degradation of the SiO_2 film continuity, even for such a thick SiO_2 film. SiO migration through the initial SiO_2 film is a limiting process during the first stages of the heat treatment (Fig. 2), but during the phosphorus diffusion, SiO_2 layer becomes a more and more open structure for the diffusion, so that the SiO

flux penetrates easier in the silicon substrate, carrying out O atoms to the silicon bulk. Near the SiO_2 /silicon interface, where the local equilibrium of reaction (1) is modified, the reverse reaction occurs.



where Si is the silicon self-interstitial atom.

Reaction (2) requires two molecules of the same type and therefore is likely to occur just near the polysilicon/ SiO_2 interface, where the SiO concentration (C_{SiO}) is sufficiently high. Reaction (2) then describes a short-range SiO_2 precipitation effect. Such a reaction determines the SiO_2 degradation on the basis of the consumption of the oxygen atom content from the SiO_2 interfacial layer. In the bulk of the FZ silicon wafers no oxygen atoms are present and therefore only reaction (1) is operative for SiO_2 precipitation.

As the phenomena described above already suggest, the existing oxygen atoms in Cz silicon wafers may influence the structural properties of SiO_2 films located between the polysilicon and silicon during the phosphorus diffusion. As it was mentioned before, a flux of SiO molecules coming from the polysilicon/ SiO_2 interface transports the oxygen atoms to the silicon substrate. In the Cz silicon wafer a flux of oxygen atoms dissolved during the growth process and coming from the silicon bulk (where the oxygen concentration C_0 is equal to the initial value C_i of the oxygen concentration) has to be taken into account [6]. We suppose for the simplicity that the oxygen concentration is lower than the critical value for the bulk precipitation (Fig. 4). An additional reaction way occurs

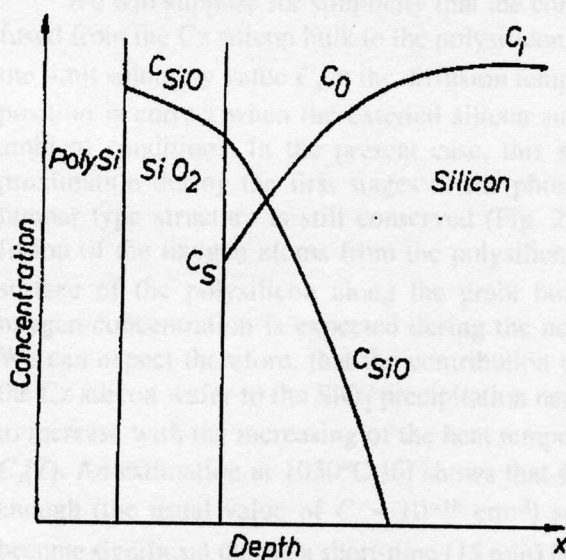


Fig. 4. - Schematic representation of the oxygen concentration and of the concentration of the SiO mobile species in Cz silicon near polysilicon/ SiO_2 interface.

under these conditions between SiO molecules escaped from reaction (2) and the oxygen atoms coming from the Cz silicon bulk:



This reaction does not contribute directly to the degradation of the initial continuous SiO₂ film, but enhances the SiO₂ precipitation process near the polysilicon/SiO₂ interface. Moreover, reaction (3) produces a long-range precipitation because of the oxygen excess in the region near the polysilicon/SiO₂ interface, which is of the order of the SiO diffusion length. Relation (3) describes then a long-range precipitation effect.

An additional enhancement of the SiO₂ precipitation in Cz silicon wafers is induced by the reaction between the bulk oxygen atoms and the silicon self-interstitial atoms coming from: (i) phosphorus diffusion in silicon substrate; (ii) phosphorus diffusion in polysilicon grains; (iii) polysilicon oxidation during the prediffusion step; (iv) conversion of SiO into SiO₂ (reaction (2)), under the form:



This reaction does not contribute to the SiO₂ film degradation, because no oxygen atoms from the interfacial SiO₂ film are used. By means of reaction (3) and/or (2), SiO₂ precipitates are generated as follows: during reaction (3) silicon self-interstitial and oxygen atoms are consumed, while during reaction (2), the silicon self-interstitials become free atoms and may participate again in to the atomic transport in silicon.

We will suppose for simplicity that the concentration of oxygen atoms diffused from the Cz silicon bulk to the polysilicon, SiO₂ interface is the same with the limit solubility value C_s^* at the diffusion temperature [6] (Fig. 4). Such a supposition is correct when the external silicon surface is exposed directly to the ambient conditions. In the present case, this supposition may be a good approximation during the first stages of the phosphorus diffusion, when the columnar type structure is still conserved (Fig. 2), because of the rapid out-diffusion of the oxygen atoms from the polysilicon/SiO₂ interface to the external surface of the polysilicon along the grain boundaries. An increasing of the oxygen concentration is expected during the next stages of the heat treatment. We can expect therefore, that the contribution of the bulk dissolved oxygen in the Cz silicon wafer to the SiO₂ precipitation near the polysilicon/SiO₂ interface to increase with the increasing of the heat temperature, depending on the values $C_s(T)$. An estimation at 1030°C [6] shows that $C_s \sim 2 \times 10^{17} \text{ cm}^{-3}$, which is high enough (the usual value of $C_i \sim 10^{-18} \text{ cm}^{-3}$) so that the precipitation process become significant during a short-time (15 min) heat treatment at 1030°C (Fig. 2).

During the phosphorus diffusion, the SiO_2 precipitation process occurs especially near the SiO_2 /silicon interface, in the short-range region. A continuous atomic transport from the SiO_2 film and from the Cz silicon bulk contributes to the SiO_2 precipitation as follows: (i) the consumption of oxygen atoms by means of reactions (1) and (2) which determine the degradation of the initially continuous SiO_2 film and the SiO_2 "regrowth" in a silicon region near the SiO_2 interfacial layer; (ii) the oxygen atoms coming from the Cz silicon bulk, determined by means of reactions (3) and (4) both the enhancement and the spatial extension (long range effect) of the SiO_2 precipitation process. The two kinds of atomic transport are related by the oxygen atoms coming from the SiO_2 film (reaction (1)) and from the Cz silicon bulk, reaction (2) and (3). The new SiO_2 formed regions will interact again with silicon self-interstitial atoms generated during the phosphorus diffusion and an additional cycle as described by reactions (1)–(4), will contribute to a further extension of the SiO_2 -precipitation region. It can be therefore explained in such a way the conversion of the SiO_2 interfacial film from 16 nm thickness (Fig. 1) to a 20 nm thickness of a SiO_2 precipitated region after 35 min phosphorus diffusion at 1030°C (Fig. 3).

5. CONCLUSIONS

The short-time (15 min) moderate temperature (1030°C) heat treatment of thick (1500 nm) LPCVD polysilicon/ SiO_2 on silicon during the phosphorus diffusion from a liquid POCl_3 source is sufficient to fully dope the polysilicon layer and to convert it in a local diffusion source. The XTEM determinations after the LPCVD deposition, phosphorus prediffusion and phosphorus diffusion allow to show that:

(1) a degradation of the initial thick SiO_2 occurs during the phosphorus diffusion at 1030°C for 15 min: the SiO_2 film is broken-up and SiO_2 precipitates are formed;

(2) a further degradation of the SiO_2 layer occurs during a phosphorus diffusion step at 1030°C for 20 min, consisting in the extension of the SiO_2 precipitation region from 16 nm after the LPCVD to 20 nm thickness after the diffusion;

(3) the SiO_2 film degradation was explained by the oxygen consumption from the SiO_2 film by means of reaction with the self-interstitial atoms mainly generated by the phosphorus diffusion and by the polysilicon oxidation;

(4) the enhancement of the precipitation process near the SiO_2 /silicon interface in the Cz silicon wafers and the extension of the SiO_2 precipitation

region was explained by the atomic transport of the oxygen atoms dissolved in the bulk of the Cz silicon wafers, diffusing to the SiO_2 /silicon interface and interacting with Si and SiO species near the SiO_2 /silicon interface.

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