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Physicochemical Characterization of Annealed PolySi/NIDOS/SiO₂ Structures

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ABSTRACT Physicochemical characterizations of polysilicon thin multilayer films have been studied after annealing. *In-situ* heavily boron-doped polysilicon (poly/Si) and nitrogen-doped silicon (NIDOS) films were deposited by low-pressure chemical vapor deposition (LPCVD) onto an oxidized monocrystalline silicon substrate. Secondary ion mass spectrometry (SIMS) profiles showed a boron diffusion reduction in the NIDOS layer. In addition, Fourier transform infrared spectroscopy (FTIR) analysis clearly showed an evolution of the absorption picks related to the nitrogen atom in the complex form leading to boron atom activation in the films. Therefore, this multilayer structure can be largely used for metal-oxide-semiconductor (MOS) devices.

KEYWORDS annealing, NIDOS, physicochemical, polysilicon

INTRODUCTION

The improvement of microelectronic components requires knowledge of the polysilicon properties used for complementary metal-oxide-semiconductor (CMOS) technology. During the past years, heavily boron-doped silicon deposited by LPCVD technique in a polycrystalline state was used as a gate for MOS transistors because it makes possible the auto-alignment of the drain and the source.^[1–3] The boron penetration can result in threshold voltage instabilities and degradation of the electrical characteristics of the gate oxide.^[4–8] Nitridation processes have been proposed to reduce the boron penetration into the gate oxide, such as nitrogen implantation, NH₃, N₂O, and NO annealing.^[9–11] In previous works, we have proposed an original solution by the insertion of a nitrogen-doped layer (NIDOS) between the polySi gate and the insulator.^[12] The main advantages of this two-layer gate engineering approach are controlling the nitrogen concentration in the 4-nm-thick NIDOS layer during the LPCVD deposition and the large grain size of the amorphous as-deposited silicon film at low temperature with disilane gas source. Gate depletion has been observed when using the standard boron implantation/annealing process to electrically activate the P+ gate, even without the NIDOS film at the interface, and boron penetration was reduced when using the NIDOS film. Then, the implantation/annealing process was not suitable for activating the polysilicon gate. In this paper, a new process is proposed by using heavily *in-situ*

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boron-doped silicon film deposited onto the NIDOS thin layer. Both the boron electrical activation, the boron diffusion into the NIDOS film, and the recrystallization of the amorphous as-deposited boron-doped silicon are presented. In this paper, we study the effect of the heat treatment of these films by performing the physicochemical characterization of multilayer thin film poly-Si/NIDOS/SiO₂ in order to optimize the annealing conditions for reliable multilayer material suitable for CMOS technology.

MATERIALS AND METHODS

Polysilicon multilayer thin films are deposited on oxidized (P-type 0.025 μm oxide thick) single-crystal silicon substrates. The two polysilicon layers were deposited in a vertical furnace by low-pressure chemical vapor deposition (LPCVD) technique at 480°C. The first layer elaborated from a mixture of disilane and ammonia (about 0.2 μm thick) was *in situ* nitrogen (1% of nitrogen content) doped (NIDOS). The second layer (about 0.13 μm thick) deposited from a mixture of disilane and boron trichloride was *in situ* boron doped (Fig. 1). These layers are thermally annealed at 700°C for different duration. Finally, the samples were characterized by two physicochemical methods. The first permits one to obtain SIMS experimental impurities concentration versus depth penetration. The profiles were recorded using a CAMECA IMS4 F instrument (Department of Electrical Engineering, INSA Toulouse, France). Moreover, the physicochemical characterization technique is used to identify the absorbance spectrum of the films in Fourier transform spectrometry analysis. FTIR was performed on an Avatar-360 spectrometer. The spectra were acquired between 4000 and 400 cm⁻¹.

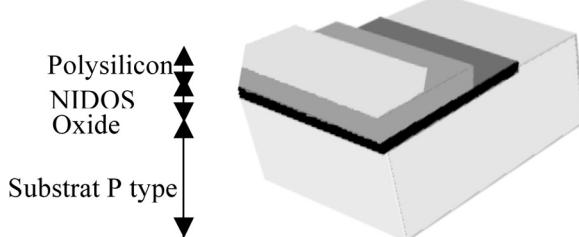


FIGURE 1 Sample structure.

RESULTS

SIMS Profiles

Figure 2 illustrates the distribution of boron impurities in multilayer film polySi/NIDOS/oxide before and after thermal annealing for 2 h duration. It should be noted that the boron peak at the poly-Si/SiO₂ interface is an artifact due to the matrix effects. The superposition of SIMS profiles shows clearly that the boron concentration remains constant (about 10²⁰ cm⁻³) in polysilicon top layer (about 0.11 μm). This can be explained by a homogeneous boron concentration during the deposition. It should be noted that under thermal annealing, the *in situ* doped polycrystalline layer is textured <110> oriented and does not rearrange significantly during the annealing,^[13] hence obtaining a very good electrical conductivity of this material.^[14] The boron concentration decreases to about 10¹⁸ cm⁻³ at the polySi/NIDOS interface region (about 0.13 μm depth) and decreases drastically to 10¹⁶ cm⁻³ in the NIDOS film (at 0.16 μm depth). Although the barrier depth is reduced, the boron does not reach the interface NIDOS/oxide. This result shows the slowing down of diffusion of boron impurities caused, on the one hand, by the amorphous layer that is fully crystallized, giving a random oriented polysilicon, and on the other hand by the presence of nitrogen in the NIDOS layer, hence the formation of the cluster or complexes that contain nitrogen atoms.^[15] This effect can be suitable to preserve the silicon oxide integrity.

IR Spectroscopy

FTIR analysis was performed on the polySi/NIDOS/SiO₂/Si structure before and after annealing. To highlight the annealing effect on the evolution of boron bonds, the FTIR spectra of the structure captured before the annealing step has been subtracted from the FTIR spectra corresponding with the annealed structure. For bonds due to the silicon oxide, the SiO₂ thickness is lower than the polySi thickness; the Si–O–Si bonds are very sensitive in FTIR but in our study do not appear because the oxide layer was subtracted. Figure 3 shows IR absorption spectra of polySi/NIDOS structure annealed at 700°C for different durations. The IR analysis highlights absorption peaks between 1400

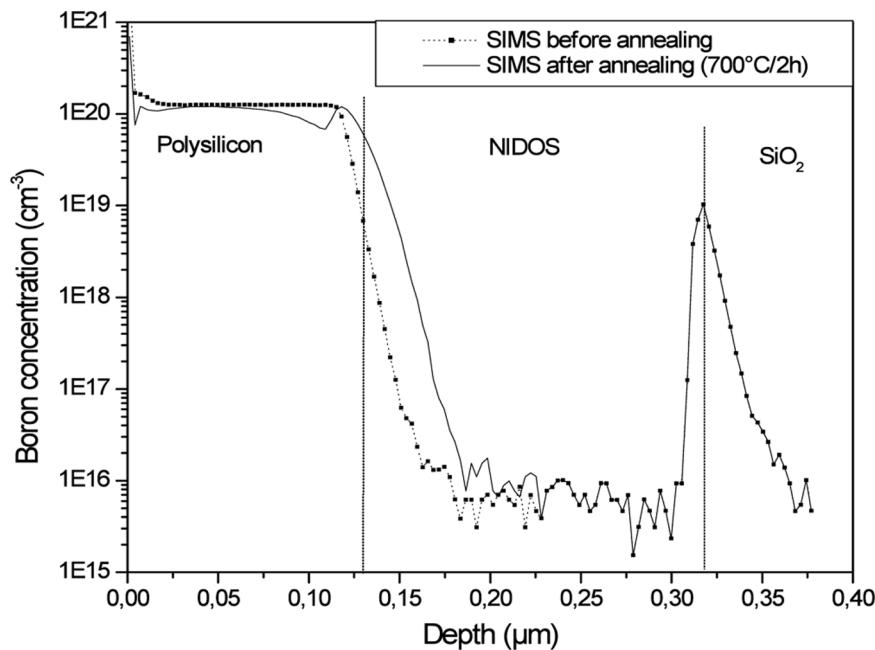


FIGURE 2 Superposition of SIMS profiles before and after annealing.

and 600 cm^{-1} . This area concerns the chemical characteristic bonds of the principal atoms present in polysilicon film (Fig. 3). The peak located around 1100 cm^{-1} corresponds with B–B bonds,^[16] and moves toward the low wavelengths as the annealing duration increases, which indicated the transformation of B–B bonds into B–N bonds located at 1083 cm^{-1} .^[17] Absorption intensities bonds that contain boron and nitrogen such as B–N (1400 and

626 cm^{-1})^[17–19] and B–N–B (750 cm^{-1})^[20], decrease with the duration increasing. In the same way, the absorption intensity of the Si–N bond located at 1250 cm^{-1} ^[21] decreases with the annealing duration. On the other hand, the absorption intensity of the Si–N bond located at 950 cm^{-1} ^[22] increases with the thermal annealing duration. This can be explained by nitrogen partial dissociation in B–N, B–N–B, and Si–N bonds, where boron atoms in polysilicon are

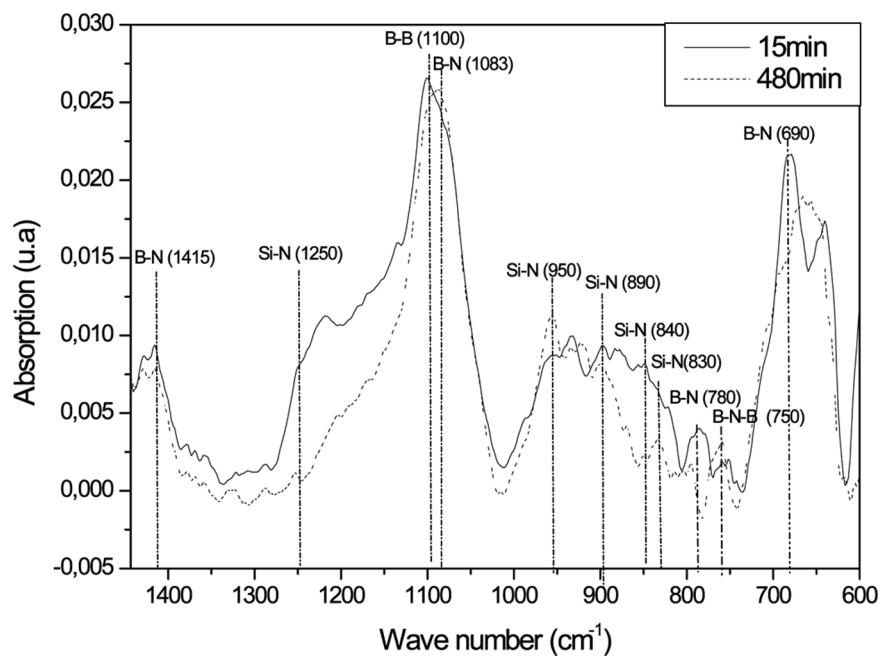


FIGURE 3 Variation of the FTIR spectra polySi/NIDOS/oxide structure with annealing.

released leading to the increase of Si–N peak intensity localized at 950 cm^{-1} . During heat treatment, the crystallization of the heavily *in situ* boron-doped polySi layer gives us a very good electrical conductivity;^[14,23] however, boron atoms penetrate quickly in the NIDOS amorphous underlying layer. The trapping of boron by the nitrogen in the NIDOS is illustrated by the presence of various bonds B–N and B–N–B. The intensity of their peaks decreases but does not disappear. Finally, this study showed that the boron atoms do not reach the NIDOS/SiO₂ interface.

CONCLUSION

The physicochemical proprieties of annealed polySi/NIDOS/SiO₂ structures obtained by LPCVD technique have been studied for MOS gate structures. The SIMS results showed clearly the boron diffusion evolution versus thermal annealing. In this structure, boron stopping in the NIDOS layer is used as barrier for boron atoms diffusion, leading to improvement of silicon gate oxide quality. The FTIR analysis results clearly showed a reduction in the absorption intensity of the bonds related to the nitrogen atom (B–N, B–N–B, and Si–N) as well as the weakening of B–B bond intensity according to the annealing conditions. This has been explained by the partial release of nitrogen and boron in silicon. The evolution of these complexes in NIDOS layer and the boron activation in polySi layer gives a good electrical conductivity of this structure. Finally, from these results, it is noted this multilayer film can be used as material for MOS gate structure.

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