EFFECT OF RAPID PHOTOTHERMAL PROCESSING ON THE C-V CHARACTERISTICS OF ANODIC SiO_2 FILMS

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Abstract. The effect of rapid photothermal processing (RPP) in nitrogen on anodic SiO_2 for high quality oxide preparation in terms of gate dielectrics in thin film transistors is reported. Samples prepared by anodic oxidation of silicon in different pre-oxidation and oxidation conditions, and RPP have been used for characterization of SiO_2 thin film devices.

Keywords: Anodic oxidation; SiO_2; rapid photothermal processing; interface traps

1. INTRODUCTION

Silicon oxide is one of the "building block" films used in metal-oxide-semiconductor (MOS) technology, comprising MOS field effect transistors (FET), which claims an important share in today's microelectronic market. This demands to grow high quality SiO_2 thin films in terms of their electrical properties and reliability. Therefore, preparation of clean Si surfaces and growth of SiO_2 thin films rapidly at lower temperatures is desired for the reliability of the device. These have to include the pre-oxidation treatment and anodic oxidation technique which has been much less explored [1].

In order to accommodate the perceived requirement for reduced thermal budgets in MOS fabrications, many approaches have been investigated to enhance post-growth annealing at lower temperatures to prepare high quality SiO_2 [2], but much attention has also been focused on the use of rapid thermal or photothermal annealing to the full fabrication process of SiO_2. Avoiding high temperature process should result in a better performance of the SiO_2 films and respectively of the fabricated devices [3]. Anodic oxidation at room temperature and post oxidation RPP can be a possible alternative to the thermal growth silicon oxide and to the conventional annealing; not only because of the low temperature process, but also because of enhanced properties obtained with the new technique of RPP.

2. EXPERIMENTAL DETAILS

The standard chemical cleaning of silicon wafers leaves behind a native unstable oxide layer [4] also various adsorbates on silicon, which affects the surface state density and the quality of the SiO_2

grown over it. Therefore non-stoichiometric native oxide and contaminants on the Si surface [5] have to be eliminated.

In the present study, the (100) silicon substrates were chemically cleaned using solution of sulfuric acid/hydrogen peroxide in the proportion 1:4 for 5 min. Then Si substrates were treated by nitric acid and after redistilled water cleaning for 5 min. The next step is cleaning in the solution of dilute ($HF:H_2O$ = 5:100) to remove chemical and native oxides, which might be formed on the surface during the 60 sec. The cleaning in solution of hydrofluoric acid also reduces contamination level to minimum at the surface, passivate the silicon dangling bonds [4] and produced a stable surface with low density of surface states. Final steps were rinsing in redistilled water and drying in N_2 jet, immediately before oxidizing process. For the second set of specimens along with the similar pre-oxidation cleaning procedure was employed, for the first time, the rapid photothermal processing of the silicon wafers, at high temperatures (900°C, 20 sec) in hydrogen ambient.

Silicon substrates of *n*-type (10 Ω·cm) after carefully pre-oxidation treatment, just before beginning of the anodic process, were attached to a holder in the anodizing apparatus. Anodic oxidations of the *n* - Si wafers have been performed under UV illumination. We used an electrolyte consisted of 0.03 M KNO_2 and 0.03 M KNO_3 in ethyleneglycol EG – 5%H_2O at room temperature. The silicon probe was connected to a constant-current source and voltage was monitored, after it had reached a predetermined value the current was allowed to decay to 0.1 $mA{\cdot}cm^{-2}$ and then disconnected. Fig. 1 shows dependence of voltage across the silicon slice during the growth process versus current density. To the silicon slice illuminated by UV light have been applied two regimes of current I_1 and I_2. In region I_1 no increase in voltage is observed during the period of current I_1 =1.0 $mA{\cdot}cm^{-2}$. Second region (I_2) represents the growth period when is applied 4.0 $mA{\cdot}cm^{-2}$. Was observed that initially the efficiency of the current is very low and a slow growth of SiO_2 and it seems this is the reason of the homogeneity. Anodic SiO_2 films thickness was measured by ellipsometry.

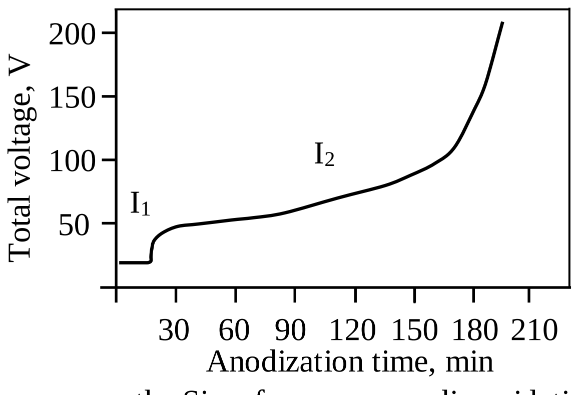

Fig. 1. Total voltage across the Si wafer versus anodic oxidation time dependence of current densities I_1 and I_2.

Post-oxidation annealing (POA) was performed in air in a quartz tube oven at precisely controlled temperature for an interval 0.5÷1.5 h. Rapid photothermal processing was performed in an IFO-6 system, the set-up detailed described in [2]. Thermal effects and quantum effects describe the photon-matter interaction. In order to compare resulting uniformity after annealing and investigate effect of RPP on the characteristics of SiO_2 films, the samples were POA in a lamp heated furnace (RPP) IFO-6 for 3, 5, 10, 15, 20 s at temperatures of 100, 200, 350, 400, 450°C. The MOS specimens have been fabricated by thermal evaporation of aluminum in vacuum system VUP-5.

Interface quality is one of the principal issues in the performance of MOS transistors and its effect is significant for thinner SiO_2 dielectrics. By analyzing the capacitance-voltage (*C-V*) curves it's possible to understand the influence of RPP on anodic SiO_2 films and the operation of MOS transistor. The C- V curves of such MOS structures using as-formed anodic oxide shown unstable behavior, and the surface state density is very high ($1\div3\cdot10^{12}$ $eV\cdot cm^{-2}$). Therefore, anodical grown SiO_2 films have been cleaned with mixture HC1 - H_2O_2 - H_2O, and annealed in an N_2 stream at different temperatures and durations using the RPP system.

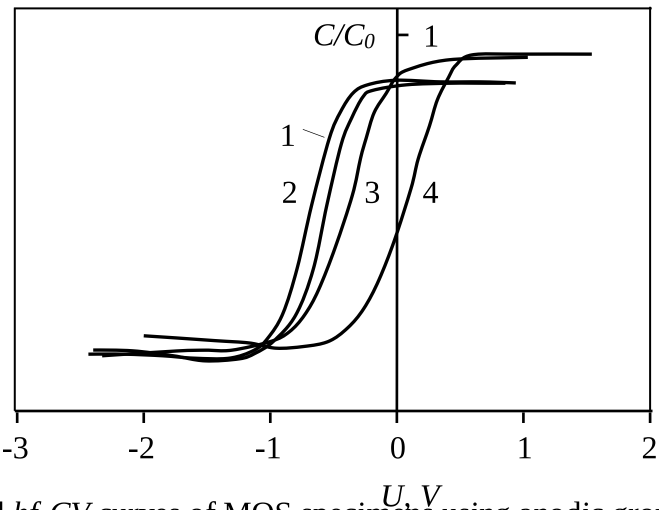

Fig. 2. Experimental *hf-CV* curves of MOS specimens using anodic grown oxide films on *n*-Si, initial (1-bath *a*, 3-bath *b*) and after rapid photon annealing (2, 4) at 450°C for 20 s in N_2 ambient, respectively.

The samples were investigated by high-frequency capacitance-voltage measurements and by the current -voltage measurements. Figure 2 shows the experimental high-frequency *C-V* characteristics of a first set of MOS specimens fabricated as described above (KNO_2 - KNO_3 in EG = bath *a*; KNO_2 - KNO_3 in EG - 5%H_2O = bath *b*), initial (1,2) and after RPP at 450°C for 20 s in N_2 ambient (3,4). Specimens with anodical SiO_2 annealed with CFA at temperatures 600, 700 and 750°C for 20 min and by RPP in IFO-6 system for 3, 5, 10, 15 s at temperatures of 100, 200, 350 and 400°C show unstable behavior and will not be discussed further in this paper. In our investigations the obtained results are adequate to illustrate that the anodic oxidation should be a promising process for SiO_2 thin films fabrications.

3. RESULTS AND DISCUSSION

The refractive indexes of the anodic SiO_2 grown under UV illumination are in the range of 1.45÷1.47 with the error of uniformity in order of 1' ÷ 20'. The variations of refractive index *n* value are determined by the modifications in the local atomic structure of SiO_2 films. The decrease of *n* value is explained by the increase in films density and by replacement of Si-Si bonds by Si-O bonds.

From *C-V* measurements of MOS specimens, it was calculated that there was a surface charge density of $5.5 \cdot 10^{11}$ electronic charges/cm^2 in as-grown anodic oxides and $1.5 \cdot 10^{11}$ electronic charges/cm^2 after rapid photo-thermal processing for 20 s at 450°C in N_2 ambient. The interface state density N_{SS} of anodic oxides is $3 \cdot 10^{11}$ eV$^{-1} \cdot$cm^{-2} before, and $5 \cdot 10^{10}$eV$^{-1} \cdot$cm^{-2} after rapid photon annealing at 450°C for 20 s in N_2 ambient.

The total amount of interface traps is generally small in the samples with KNO_2 and KNO_3 ethyleneglycol mixture-anodic oxide used as the gate dielectrics. The RPP anneals the traps in the oxide but at the same time they depend on technological history of the samples (pre-oxidation treatment, anodization conditions and POA) and the anodic oxide quality. As there is no higher temperatures (> 700°C) process involved and the oxidation was performed in a slow fashion, the number of oxidation-induced defects can be minimized using this method.

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