Available online at www.sciencedirect.com
ScienceDirect
Vacuum 82 (2008) 1020–1028
VACUUM
SURFACE ENGINEERING, SURFACE INSTRUMENTATION & VACUUM TECHNOLOGY
www.elsevier.com/locate/vacuum

Application of r.f. plasma ultrashallow nitrogen ion implantation for pedestal oxynitride layer formation

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Abstract

The study examines the possibility of fabrication of pedestal oxynitride layers for high-k gate stacks by means of nitrogen implantation from r.f. plasma alone or followed immediately by the plasma oxidation process.

The obtained layers were characterized by means of ellipsometry, X-ray photoelectron spectroscopy (XPS) and ultra low energy secondary ion mass spectrometry (ULE-SIMS). The results of electrical characterization of NMOS Al-gate test structures fabricated with the investigated layers used as a gate dielectric are also discussed.

Presented results seem to be very promising and presented methods allow to form ultrathin pedestal oxynitride layers with good properties (e.g. breakdown behavior) and we believe that presented method—ultrashallow nitrogen plasma implantation with plasma oxidation may be seriously considered for future VLSI technologies.

Keywords: CMOS; Gate stack; Pedestal oxynitride; Plasma implantation

1. Introduction

According to the ITRS roadmap [1] the thickness of the gate dielectric layer will be dramatically reduced in the near future (<1 nm in 2011). Such extremely thin layers generate, however, a lot of problems in terms of processing repeatability and reliability. This, in turn, creates a pressure to substitute silicon dioxide with a single layer of high-k material or—more probably—with a gate stack (a combination of high-k material and a pedestal layer passivating silicon–dielectric interface).

Oxynitride layers seem to be very promising in this respect. This is mostly due to the fact that silicon nitride layers are known to be very resistant to diffusion and thus, also to oxidation, while oxide is undisputedly the best possible passivating layer for silicon surface.

Oxynitride layers can be produced with a number of methods. Presented experiments are a study that examines the possibility of fabrication of pedestal oxynitride layers by nitrogen implantation from r.f. plasma (denoted hereafter as "as-implanted") or nitrogen implantation from r.f. plasma followed immediately by plasma oxidation process.

Differently to the methods presented in the literature so far [2,3], where the classical implanters or the ion immersion implantation in plasma (IIIP) technique were used for implantation, in this work we used a typical r.f. plasma planar reactor, usually applied for the PECVD (Oxford Plasma Technology—Plasmalab 80 Plus). The obvious advantage of our approach is that while equipment for III is rare and can hardly be found in typical silicon technology laboratory—the planar reactors for PECVD are practically in each of them.

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doi:10.1016/j.vacuum.2008.01.010

2. Experimental

In this work, ultrashallow plasma implantation of nitrogen ions and low temperature plasma oxidation were used to form the ultrathin pedestal oxynitride layers. Both these processes were performed in a classical PECVD reactor. The investigated layers were formed under different process conditions. The variable process parameters were: implantation time, r.f. power, nitrogen source gases, and temperature. A detailed process description may be found in [4–6].

A two-stage analysis of the studied ultrathin oxynitride layers was performed. In the first stage, the layers formed with the nitrogen plasma implantation only (as implanted) were characterized in order to understand the state of the silicon substrate right after the plasma implantation. In the second stage, the layers formed with the nitrogen implantation followed by plasma oxidation underwent a similar analysis, to understand the consequences of the complex process.

Structural properties of the investigated layers were during this study characterized by ellipsometry, X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) [7–9].

For the ellipsometry measurements a GAERTNER 118 (632.8 nm) ellipsometer and spectroscopic ellipsometer VASE J.A. Woollam ($\lambda = 250$–1000 nm) were used.

The XPS measurements were performed in the Brandenburg Technical University (Cottbus/Germany). Typically used energy was Mg Kα—1253.6 eV [10–19] and for all investigated layers full spectrum and in detailed Si2p, N1s and O1s peaks were measured. Thicknesses of the layers were calculated by Tanuma calculations [8].

The SIMS measurements (with Ar^+ ultra low energy source—880 eV) in turn, were performed using setup available in the Industrial Institute of Electronics/Warsaw [20,21].

Structural analysis was aimed at independent determination of the chemical composition and thickness of the layers. Electrical measurements of NMOS test structures with the investigated layers used as gate dielectrics were also performed.

The NMOS test structures were then electrically characterized by means of C–V and I–V measurements in order to evaluate: effective charge density, charge trapping, leakage currents and breakdown behavior.

3. Results and discussion

In the first step, analysis of the correlation between the ultrashallow plasma implantation parameters and composition and thickness of the affected silicon layer was made.

The following parameters of the plasma implantation were of the interest in this work: type of nitrogen source gas, r.f. plasma power, implantation time and sample temperature during implantation.

The XPS studies have revealed that although during implantation either nitrogen or ammonia plasma were used, the implanted substrate region consisted mostly of silicon dioxide. This must be the result of a spontaneous oxidation upon the exposure of the samples to the atmosphere when removing them from the plasma reactor after implantation. Even though the implantation temperature is only 200 or 350 °C—the results prove that the implantation leaves the silicon surface very prone to oxidation even in such unsually unfavorable conditions.

There are, however, small differences in the composition of the studied layers depending on the nitrogen source (see Fig. 1).

Marginally higher content of nitrogen is observed for nitrogen implantation from ammonia plasma. Different nitrogen content and/or damage caused to the silicon surface during nitrogen implantation result in significantly different overall layer thickness—lower for implantation from ammonia than from nitrogen plasma. Thus, it seams reasonable to choose ammonia plasma for the purpose of formation ultrathin pedestal layer. The second phase of the work reported below (complex implantation/oxidation studies) has been based on this conclusion.

From the reference experiment in which the silicon sample was subjected to Ar plasma bombardment (for the same as in case of nitrogen and ammonia plasmas r.f. power—100 W) one can justify the influence of substrate damage caused by bombarding ions. Comparison of the thickness of spontaneously oxidized layers after their exposure to either argon or nitrogen plasma clearly proves that the nitrogen presence in the surface silicon layer significantly slows down the oxidation rate.

This, in turn, proves that the presence of nitrogen-rich oxide at the silicon surface may be effectively used to prevent, or at least to reduce, oxide growth at the silicon interface during high-k dielectric deposition and/or source and drain dopant activation annealing.

The next correlation to investigate was the influence of implantation r.f. power. The analysis based on the example of NH_3 samples shows that r.f. power is a very important process parameter (see Figs. 2 and 3). Increasing implantation power results in a decrease of the layer thickness and in minor changes of its chemical composition (see Fig. 2). It is not obvious if these changes are sufficient to cause the observed reduction of the layer thickness. The other possibility is that changing r.f. power affects the density of the plasma and thus—also the implantation and substrate damage efficiency, which in turn can lead to a change in spontaneous oxidation rate. Additional data for this analysis may be obtained from ultra low energy secondary ion mass spectrometry (ULE-SIMS).

Analysis of ULE-SIMS data yielded similar results to the ones obtained from XPS. They prove that r.f. power used for nitrogen implantation is a crucial process parameter. As can be clearly seen in Fig. 3, depending on r.f. power used, the maximum of the nitrogen profile may be located just below the surface of the layers (for power not