ELSEVIER

XPS study of pulsed Nd:YAG laser oxidized Si

G. Aygun [a,b,*], E. Atanassova [c], K. Kostov [d], R. Turan [a]

[a] Department of Physics, Middle East Technical University, TR-06531, Ankara, Turkey
[b] Department of Physics, Izmir Institute of Technology, TR-35430, Urla-Izmir, Turkey
[c] Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia 1784, Bulgaria
[d] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Abstract

X-ray photoelectron spectra (XPS) of thin SiO_2 layers grown by pulsed Nd:YAG laser at a substrate temperature of 748 K are presented. The peak decomposition technique combined with depth profiling is employed to identify the composition and chemical states of the film structure. It is established that the oxide is non-stoichiometric, and contains all oxidation states of Si in different amounts throughout the film. The interface Si/laser-grown oxide is not abrupt, and the coexistence of Si_2O_3 and Si_2O suboxides in a relatively wide interfacial region is found. It is concluded that post-oxidation annealing is necessary in order to improve the microstructure of both oxide and near interface region.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

The great success of microelectronics, during the past several decades is related with the fact that Si has native oxide that is SiO_2 – nearly ideal insulator giving practically perfect interface with Si. The continual scaling of CMOS technologies, however, has pushed the Si/SiO_2 system to its very physical limits and the development of future generations (Gigabit scale) of both Dynamic Random Access Memories (DRAMs) and MOSFETs require alternative dielectric films with a high dielectric constant, (high-κ) [1–3]. At the same time, new methods of oxidation of Si for extremely thin SiO_2 growth is still a subject of ongoing investigations [4–8]. These methods are in fact new trends in the efforts to obtain dielectric (mainly SiO_2-based) layers with enhanced capacitance properties to meet the requirements of the high density DRAMs. Among them, the tech-

niques enabling local and low temperature oxidation are of a special interest. For example, the local oxidation by Atomic Force Microscopy (AFM) has received much attention [5,6]. At present, however, AFM-grown SiO_2 shows very poor dielectric quality compared to thermally grown SiO_2 [6] and is not suitable as an active dielectric. It is not convenient for mass production either. Despite the fact that the techniques of laser oxidation are far from their full optimization, they have a great potential for future device applications. In addition to the advantages such as local oxidation and low processing temperatures, laser-assisted oxidation provides a good control over the thickness of very thin films including SiO_2 [7,9–12]. Recently, we have reported [7,13] that the amorphous thin SiO_2 films could be successfully obtained by pulsed Nd:YAG laser in O_2 ambient at relatively low temperatures. It was established that an interval of laser beam energy density exists in which the oxidation occurs without surface melting. Electrical data of laser-oxidized SiO_2 layers have shown typical MOS behavior and the laser-grown

* Corresponding author. Tel.: +90 232 750 7637; fax: +90 232 750 7509.
E-mail address: aygun@photon.iyte.edu.tr (G. Aygun).

oxide generally has parameters close to those of thermally grown SiO_2 in terms of interfacial defect charges, slow state densities and leakage current levels. The results implied, however, that the oxide through the depth is most likely non-stoichiometric, with excess Si. It was speculated that the structural non-perfections are responsible for the detected high density of oxide charge. Obviously, the precise structural analyses are required for laser-oxidized films. It is known that X-ray Photoelectron Spectroscopy (XPS) could be successfully used to detect as well as to identify various suboxides and their distribution in the oxide and at the interface. In this article, XPS investigation of laser-oxidized SiO_2 is reported. The best oxidation conditions in terms of laser beam energy density and substrate temperature are used as determined by the capacitance–voltage and current–voltage characteristics [7]. Layers with thickness d of 40 nm were studied.

2. Experimental procedure

Chemically cleaned p-type (1 0 0) 15 Ωcm Si wafers (a standard 2:1 solution of H_2SO_4 and H_2O_2) were used as substrates. After the cleaning (including the final step of dipping into dilute HF to remove the native oxide), the samples were laser oxidized in vacuum chamber evacuated to a base pressure below 0.13 Pa. The substrate was heated to the temperature of 748 K prior to oxidation. O_2 gas was introduced into the chamber (working gas pressure, p, was 123 Pa) after reaching the desired substrate temperature. Nd:YAG laser at 1064 nm, (EKSPLA Pulsed Laser NL 301) was used to induce oxidation. The laser output is composed of a pulse train with individual pulses typically of 4.7 ns. More details on the laser parameters and the process of oxidation can be found elsewhere [7]. The approach used is only briefly described here. A computer controlled X–Y scanner system was used to direct the laser beam on a certain region on the substrate with controllable dimensions. By means of the scanner system, the laser beam was scanned over an area of the substrate of approximately 4×4 mm^2 and it can be further reduced by the software. The laser beam energy density, P, was 3.4 J/cm^2 per pulse. The preliminary measurements showed that the small variations of P, from 3.35 to 3.45 J/cm^2, had no effect on the XPS data. According to the previous results [7], this value of P is close to the laser fluence corresponding to surface melting but without crossing it. It enables oxidation process without surface melting. The oxide thickness and refractive index of the layers obtained were measured by ellipsometry ($\lambda = 632.8$ nm). The refractive index was 1.45.

XPS was used to analyze the composition and chemical states of laser-oxidized SiO_2 film and its interface with Si. The data were obtained using an Al K$_\alpha$ (1486.6 eV) excitation source in ESCALAB Mk II apparatus (VG Scientific) with a residual gas pressure better than 1×10^{-8} Pa. All spectra were taken at 300 K. The photoelectrons were separated by a semispherical analyzer with a pass energy of 10 eV and an instrumental resolution of 1.0 eV measured

as the Full Width at Half Maximum (FWHM) of the Ag $3d_{5/2}$ photoelectron peak. The energy position of the peaks was determined with an accuracy of 0.1 eV. The photoelectron lines of Si 2p and O 1s were recorded. The binding energies E_b have been corrected for sample charging effect with referenced to the C 1s line at 285.0 eV for the surface of the oxide, and to the Si 2p line of the elemental Si at 98.7 eV for all spectra obtained after ion sputtering. The peak positions and FWHM were determined from least square fitting using the instrument's software. The peak shapes for all peaks were fixed to a mix of Gaussian–Lorentzian functions. The final fitting was made iteratively. The composition was calculated using the standard software. The spectra were obtained under the angle of 90°, (with respect to the surface plane) of photoemitted electrons. The chamber was also equipped with an ion source to facilitate in situ sputtering of the sample by Ar$^+$ to determine the concentration profiles of various species. The argon ion beam was with an energy of 1.5 keV and a current density of 12 μA/cm^2. The angle of incidence of the sputtering beam was 40° with respect to the surface of the layer. The experimental curves are as-recorded data after Shirley background subtraction. It is very important to minimize the adverse effects of the ion beam on the sample stoichiometry during the ion sputtering. It is known [14] that 1–1.5 keV argon ions sputter conventional SiO_2 keeping its stoichiometric ratio, i.e., the ions remove Si and O at a rate very close to 1:2. Therefore, we assume that eventual unfavorable effects of the ion beam sputtering such as a preferential sputtering should not influence considerably the experimental results and conclusions drawn from them. During sputtering the structure of the SiO_2 layer is likely to be damaged but this is not reflected on the Si 2p binding energy or its line width. For sputtering times, t_s, of 0.5–140 min, the thickness reduction as measured by XPS [15] was linear with t_s and the sputtering rate was obtained to be 3 Å/min. The sputtering rate determined by the measured oxide thickness and t_s was approximately the same, (2.9 Å/min) indicating that both methods are correct.

3. Results and discussion

3.1. Si 2p spectra

Fig. 1 presents the variation of the experimental Si 2p spectra through the depth of the films, (d_0 is the distance from the surface). The spectrum at the surface reveals a peak in the C 1s region (not shown in the figure) with negligible intensity demonstrating that the surface remains clear enough after short air exposure. The carbon signal (at 284.6 eV, indicating the presence of C–C bond) is due to adsorbate which disappears when surface is sputtered slightly, ($t_s \sim 0.5$–1 min). Fig. 2(a)–(d) illustrates spectra for several selected distances from the surface. The solid line represents as-recorded data. The peak positions extracted from the depth spectra, FWHM of the peaks