Characterization of ultrathin SiO_2 films formed by direct low-energy ion-beam oxidation

C. F. Yu, S. S. Todorov, and E. R. Fossum
Columbia Radiation Laboratory and Department of Electrical Engineering, Columbia University, New York, New York 10027

(Received 19 September 1986; accepted 8 December 1986)

Bombardment of silicon (100) surfaces at room temperature by an oxygen-containing low-energy ion beam is studied as an alternative to thermal oxidation to produce ultrathin oxide films. A self-limiting oxide thickness of about 50 Å is obtained by using ions with energy 100 eV or lower. Auger electron spectroscopy depth profiles of an ion-beam grown oxide and a thermally grown oxide show very similar composition. Grazing angle x-ray photoelectron spectroscopy indicates the presence of lower oxides of silicon near the surface. The capacitance–voltage characteristics of ion-beam grown oxides compare favorably with those of thermally grown oxides.

I. INTRODUCTION

Ultrathin gate oxide films are expected to gain increasing importance as metal–oxide semiconductor (MOS) devices are scaled to smaller dimensions. At the same time, low-temperature processes are already replacing many thermal fabrication steps in an attempt to minimize damage to the substrate. Many processes have been proposed as low-temperature alternatives to thermal oxidation of silicon, the most notable being plasma oxidation and chemical vapor deposition (CVD).[1–3] These methods, however, have not yet produced thin oxides suitable for MOS applications. We have studied the bombardment of (100) silicon surfaces by oxygen-containing ion beams and have successfully grown ultrathin device-quality oxides.[4]

The composition of the obtained ultrathin oxides is analyzed by Auger electron spectroscopy and x-ray photoelectron spectroscopy. The oxides are also characterized electrically by studying the capacitance–voltage (C–V) and current–voltage (I–V) characteristics of aluminum-gate MOS capacitors.

II. EXPERIMENTAL METHOD

Low-energy ion-beam oxidation uses a 2.5-cm-diam single-grid Kaufman-type source which produces a Gaussian ion beam with energies up to 100 eV. The maximum beam current density at the target is 150 μA/cm^2. The source uses argon and oxygen gases in varying ratios with an oxygen partial pressure in the low 10^{-4} Torr.

Ion-beam oxide MOS capacitors are fabricated on wafers which have a 5000-Å wet oxide grown at 950 °C and annealed for 30 min at the same temperature in dry N_2. The ion beam is then used to grow ultrathin gate oxides in windows etched in the thick oxide. The wafers are unheated; a thermocouple mounted on the substrate holder indicates typical temperature rises of < 5 °C above room temperature. Aluminum is evaporated and patterned to form the capacitors. After metallization the sample is annealed in forming gas at 400 °C for 5 min.

Control samples of MOS capacitors with thermally grown gate oxides are fabricated according to the same procedure. Here the gate oxides are grown in dry oxygen at 900 °C and annealed *in situ* in nitrogen.

Samples for surface analysis are prepared according to the same procedure without the aluminum deposition. Surface analysis was performed using a multiprobe surface spectroscopy system equipped with a concentric hemispherical energy analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out with the Mg K_α line (1253.6 eV) at 240 W. The system was calibrated from the Au $4f_{7/2}$ level with a binding energy of 83.8 eV. C 1s from residual carbon on the surface was verified to have binding energy 284.6 eV to eliminate any charging effects. Auger electron spectra were taken with a 3-keV electron beam with a 1-mm spot size on the surface. A differentially pumped ion gun was used to generate 3-keV argon ions to sputter the surfaces. The typical ion current density used was 1.2 μA/cm^2. The system pressure was kept below 5×10^{-10} Torr for XPS and 5×10^{-8} Torr for Auger electron spectroscopy (AES) and maintained at 2×10^{-7} Torr in argon while sputtering.

III. RESULTS AND DISCUSSION

Auger electron spectroscopy in conjunction with argon ion sputtering is used to study the depth profile of the oxide layer. As shown in Fig. 1, the O(KLL) and Si(LVV) Auger

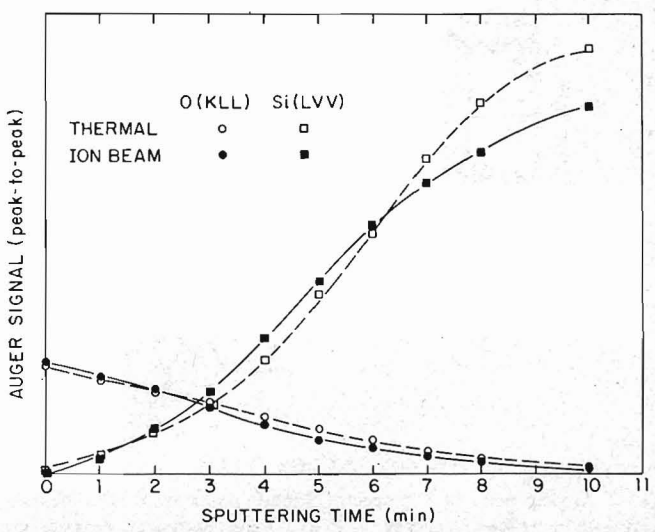

FIG. 1. AES depth profiles of thermally grown and ion-beam grown oxides.

 0734-2101/87/041569-03$01.00

peak-to-peak signals are plotted as a function of sputtering time for both an ion-beam grown oxide and a thermally grown oxide about 50 Å thick as measured by ellipsometry. For the Si (LVV) emission only the signal from the substrate is shown because of the greater sensitivity. The close resemblance of the two depth profiles indicates that the ion-beam oxide is of comparable composition to the thermally grown oxide, except that the latter has a somewhat sharper interface. Because of the limited depth resolution the actual interface for both samples is much sharper than it appears.

Angle-dependent x-ray photoelectron spectra of the ion-beam grown oxide are shown in Fig. 2 for increasing detector angles. θ is the angle between the detector axis and the surface normal. At low detector angles the Si $2p$ (SiO_2) signal is peaked at 102.9 eV, a typical value observed for very thin SiO_2.[5] However, at $\theta = 80°$ where the electron escape depth is about 5 Å, the peak position is shifted to 102.1 eV. This indicates the presence of lower oxides in the top few layers due either to the preferential sputtering or to the low mobility of the oxygen atoms incorporated in the film. The O 1s peak has an unresolved component which grows in relative proportion toward higher detector angle and is shifted toward lower binding energy by about 1.2 eV. It has been shown that the O 1s peak due to lower oxides in ultrathin thermally grown SiO_2 does not shift more than 0.3 eV.[6] Therefore, this component is probably associated with the radiation damage caused by the ion bombardment. Large sample size was used to avoid the projection loss at grazing angle. The large decrease of intensity at $\theta = 80°$ is probably due to misalignment of the detector axis and the sample rotation axis. Both the O 1s and Si $2p$ (SiO_2) peaks from the thermally grown oxide (not shown here) appear to be sharper than the ones from the ion-beam oxide and their shapes do not change at higher detector angles.

Figure 3 compares the C–V and I–V characteristics of a

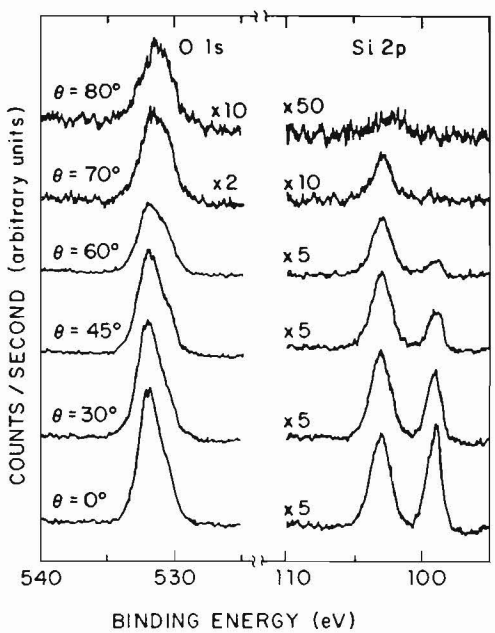

FIG. 2. Angle-dependent XPS spectra of ion-beam grown oxide. The Si $2p$ peak with lower binding energy ($\sim$99 eV), which disappears near grazing angle, corresponds to the substrate. The peak with higher binding energy ($\sim$103 eV) corresponds to the oxide.

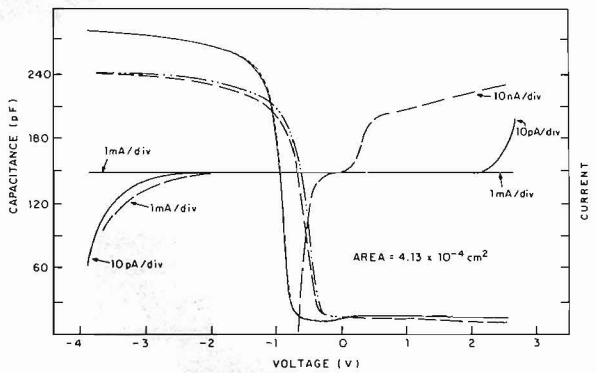

FIG. 3. Comparison of high-frequency capacitance–voltage and current–voltage characteristics for MOS capacitors with thermally grown (solid lines) and ion-beam grown (dashed lines) gate oxides.

capacitor with an ion-beam grown oxide and a thermally fabricated capacitor. The thickness of the ion-beam oxide is 56 Å; the thermal oxide is 52 Å thick. The ion-beam oxide is grown using a 100-eV ion beam with a 125 μA/cm^2 maximum current density at the target. The Ar:O_2 ratio in the source is 1:1. The sample is exposed for 6 min leading to a maximum dose of 2.8×10^{17} cm^{-2}.

The I–V curves clearly show that the ion-beam oxide passes some current—in reverse bias its leakage current is three orders of magnitude greater than the thermal oxide leakage current. This may be due to a combination of higher thermal generation rates and a lower oxide impedance. Note, however, that the leakage current through the oxide does not hinder the proper functioning of MOS transistors fabricated with ion-beam gate oxides.[7] The leakage current is more than three orders of magnitude smaller than the drain–source saturation current.

A comparison of the C–V curves, however, is much more favorable. Note that the characteristics are similarly steep in depletion and in the sharp onset of inversion. The small hysteresis of the ion-beam sample indicates the presence of some interface states. Quantification of the interface states is difficult due to the large leakage current. The threshold voltage shift of the ion-beam oxide is also indicative of uncompensated damage to the oxide or substrate. The behavior of the ion-beam oxide in inversion is easily understood from the I–V curves—the deep depletion is due to some of the inversion layer charge leaking away. The observed rise in the C–V characteristics in inversion is believed due to the coupling of minority carriers from surrounding inverted regions under the field oxide.

IV. SUMMARY

Low-energy ion-beam oxidation at room temperature has successfully produced ultrathin films of silicon dioxide suitable for use in MOS devices. The obtained film composition is comparable to that of thermally grown ultrathin oxide films.

ACKNOWLEDGMENTS

This work was supported by the Joint Service Electronics Program under Contract No. DAAG29-85-K-0049 and the IBM Postdoctoral Fellowship Program.

[1]T. Roppel, D. K. Reinhard, and J. Asmussen, J. Vac. Sci. Technol. B **4**, 295 (1986).
[2]S. I. Kimura, E. Murakami, T. Warabisako, H. Sunami, and T. Tokuyama, IEEE Electron Device Lett. **7**, 38 (1986).
[3]A. K. Ray and A. Reisman, J. Electrochem. Soc. **128**, 2424 (1981).
[4]S. S. Todorov, C. F. Yu, and E. R. Fossum, Vacuum **36**, 929 (1986).
[5]P. J. Grunthaner, M. H. Hecht, F. J. Grunthaner, and N. M. Johnson, J. Appl. Phys. **61**, 629 (1987).
[6]R. Flitsch and S. I. Raider, J. Vac. Sci. Technol. **12**, 305 (1975).
[7]S. S. Todorov, S. L. Shillinger, and E. R. Fossum, IEEE Electron Device Lett. **7**, 468 (1986).