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Direct formation of dielectric thin films on silicon by low energy ion beam bombardment

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Dielectric films with thickness of the order of 50 Å are obtained at room temperature by bombarding exposed silicon surfaces with an oxygen-containing ion beam of energy 60 eV. Silicon nitride thin films have also been formed using the same technique. The film thickness is self-limited and largely independent of ion dose. AES and XPS analysis of the produced thin films indicate that the films are not entirely stoichiometric and contain lower oxidation states of silicon. The high electrical quality of the oxide films is demonstrated by the successful fabrication of n-channel MOS transistors with gate dielectrics obtained by ion beam oxidation at room temperature.

Introduction

Silicon dioxide is an indispensable material for silicon MOS technology where its excellent dielectric properties are used both for insulation and field enhancement in the finished devices and at various stages of the fabrication process. Oxides for such applications are usually grown on the surfaces of silicon wafers in oxidizing ambients at temperatures exceeding 900°C. In some applications, such as thin-film FETs on low-melting point substrates, e.g. for flat panel displays, an alternative to thermal oxidation must be found. Reduced-temperature oxidation is also desirable in conventional silicon technology since repeated heating and cooling of the substrate leads to thermal stresses, crystal defects, wafer warpage and impurity redistribution. These become increasingly important with the trend toward smaller device dimensions and the efforts to fabricate stacked three-dimensional MOS structures.

Various techniques have been proposed for oxidation of silicon at reduced temperatures, including plasma oxidation and anodization, chemical vapour deposition (CVD) and plasma-enhanced CVD, reactive sputtering, evaporation or sputtering in an oxygen ambient, and a number of other methods. However, few of these have successfully produced thin oxides suitable for gate dielectrics. Recent reports of successful MOSFET fabrication using oxidation at reduced temperatures include microwave plasma oxidation at 580°C[1], plasma oxidation at 500°C[2] and rf sputter deposition at 200°C for 10 h[3].

In this paper, we report on the use of a broad low-energy ion beam for direct formation of ultra-thin device-quality oxide and nitride films on silicon. The method has allowed the first successful fabrication of FET-quality thin oxides at room temperature. Low energy ion beam oxidation has the added advantage of being a clean vacuum process with independent control over the process parameters and compatibility with other ion beam or vacuum techniques.

Broad low-energy ion beams have previously been applied to the oxidation of metals for fabrication of superconducting[4] and MOM[5] structures and for investigation of reaction kinetics in reactive near-threshold sputtering[6]. Focused ion beams have also been used to study the oxidation kinetics on (111) silicon[7].

Fabrication

The experiments were performed using a single-grid Kaufman-type ion source, shown schematically in Figure 1. The source produces a 2.5 cm dia ion beam and is capable of extracting comparatively large current densities at low applied voltages. The extracted ions impinge on an electrically grounded target positioned 15 cm from the source on a copper substrate holder

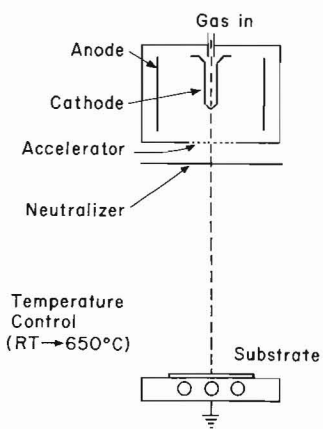

Figure 1. Schematic diagram of low energy ion beam experimental set-up. Base pressure: 3×10^{-7} torr.

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whose temperature is monitored by a surface mounted thermocouple. The target temperature is observed to rise only several degrees above room temperature during ion beam treatment.

To demonstrate the high electrical quality of the ion beam grown thin dielectrics, MOS transistors were fabricated using the following procedure on 5 cm dia (100) 5 Ω cm p-type silicon wafers, polished on one side. The wafers are chemically cleaned in degreasing agents, H_2SO_4:H_2O_2 and 10% HF. p^+ channel stops and n^+ source and drain junctions are formed by high-temperature (1050°C) diffusion of boron and phosphorus, respectively, from spin-on sources through oxide masks prepared by oxidation in steam at 1000°C. A 5000 Å field oxide is grown under the same conditions and gate regions are etched through to the silicon surface using a standard wet buffered oxide etchant (BOE). Immediately before ion beam treatment the wafers are dipped in a cold dilute HF solution to remove any residual native oxide from the gate regions. After ion beam treatment, contact holes are opened through the thin dielectric and 3000 Å of aluminium is evaporated and patterned to form the contact metallization. Then, 3000 Å of aluminium is evaporated on the backside of the wafer to form a substrate contact. Brief post-metallization annealing is carried out for 3 min in N_2 at 400°C.

To investigate the thickness of the thin films, experiments were also performed on simpler substrates on which only MIS capacitors were fabricated according to the above procedure except no p^+ and n^+ regions were diffused and no contact holes were etched. These wafers also have large bare regions free of devices used to verify the thickness of the films by ellipsometry measurements.

To ensure that the deposited films are grown by direct ion bombardment and are not due to redeposition of material sputtered from portions of the wafer covered by the field oxide, ion beam oxidation was also carried out on bare silicon wafers cleaned and dipped in HF following the same procedure. The film thickness of these samples was measured on a Gaertner Model L117 ellipsometer immediately after ion beam bombardment and over a period of several days to ensure stability of the deposited films. These samples were also characterized by Auger electron spectroscopy and by XPS in a Leybold-Heraeus LHS-10 surface analysis system equipped with a hemispherical mirror analyser. The base pressure in the characterization chamber is 4×10^{-10} torr. Sputter profiling of the samples is done at 1×10^{-7} torr argon.

Results and discussion

The dependence of the film thickness obtained by ellipsometry on the duration of ion beam treatment is shown in Figure 2. Values for the oxide thickness were also obtained from the accumulation capacitance of MIS capacitors measured after post-metallization annealing. The oxide thickness calculated from *C–V* measurements before annealing is unreliable due to series resistance in the evaporated aluminium–substrate contacts.

The ellipsometry measurements indicate that after a rapid initial growth rate, the oxide thickness increases very slowly with increasing exposure times. This can be explained by the very limited diffusion of oxygen atoms in the silicon at this low temperature and the inability of fresh oxygen arrivals to reach unreacted silicon. It should be noted that the thicknesses obtained from the *C–V* measurements are all consistently slightly higher than the values obtained by ellipsometry. This is probably due to amorphization of the thin film by the bombarding ions which

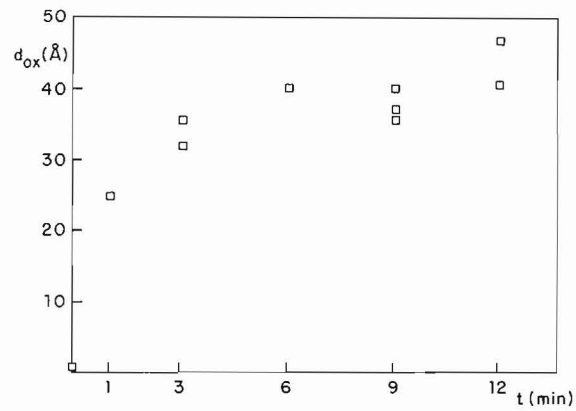

Figure 2. Oxide layer thickness obtained by ellipsometry as a function of ion beam exposure. O_2 partial pressure: 6.5×10^{-5} torr. Ion energy: 60 eV.

would lead to the films having a different dielectric constant than that of bulk SiO_2 which is assumed in the calculations of the thickness based on *C–V* measurements.

This figure is a good illustration of the self-limiting behaviour of the obtained thin films. Self-limitation was observed in the measurements of the resistance of thin films grown by direct ion beam oxidation of nickel[5] and for etch depths obtained by reactive sputter etching[8], where the self-limitation is believed due to the competing effects of deposition and sputtering.

This dose independence has the useful property of producing very uniform oxide thickness across large targets. The uniformity of the oxides is shown in Figure 3 where it is plotted against the ion beam intensity profile. The oxide thickness is obtained from the accumulation capacitance of 2.8×10^{-3} cm^2 MOS capacitors at various wafer sites. The ion beam intensity is measured by a 1.13 cm dia current probe.

Figure 4 follows the evolution of the Si (LVV) and O (KLL) peaks in the Auger spectrum of an ion beam oxide and a thermal oxide measured by ellipsometry at 47 Å and 48 Å, respectively. The thermal oxide sample was prepared by placing a cleaned silicon wafer in a pure dry oxygen atmosphere at 900°C for 8 min. AES is performed with a 3 keV electron beam having a 1 mm spot size at the target. Profiling is accomplished by sputtering the

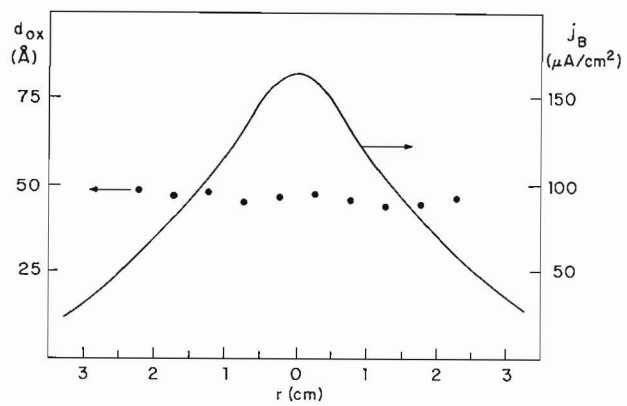

Figure 3. Comparison of oxide thickness uniformity across a 5 cm Si wafer (from *C–V* measurements of 2.43×10^{-3} cm^2 MIS capacitors) and ion beam current density profile at the target. Current density probe diameter: 1.13 cm. O_2 partial pressure: 6.5×10^{-5} torr. Ion energy: 60 eV. Exposure time: 6 min. Accelerating voltage: 20 V.

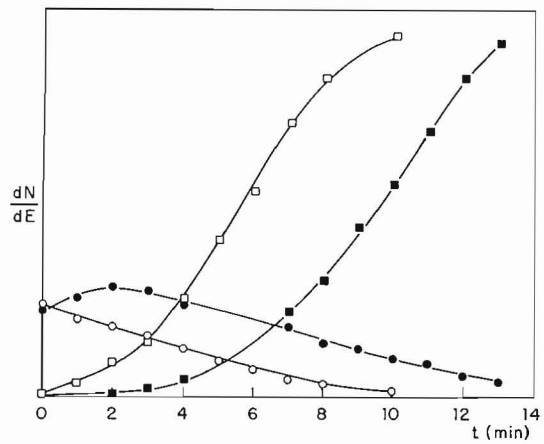

Figure 4. Depth profiles of thermal and ion beam oxides. Plotted are the peak-to-peak amplitudes of Si (LVV) and O (KLL) Auger signals. □—thermal Si; ○—thermal O; ■—ion beam Si; ●—ion beam O.

sample with a differentially pumped rastering 3 keV argon ion source with current density 1.2 μA cm^{-2}. Based on ellipsometry, the sputtering rate for SiO_2 is 3.5 Å min^{-1}. The depth profile of the thermal oxide indicates a linearly decaying signal corresponding to uniform composition of the film. The oxygen profile for the ion beam oxide has a peak at a depth of about two monolayers. This, as well as the attenuation of the silicon signal would indicate higher concentration of impurities near the surface. The complete surface Auger spectrum contains a tungsten peak due to sputtering of the source cathode and neutralizer filaments. The shallower slope of the concentration profiles in the ion beam sample compared to the thermal oxide would also indicate a larger width of the interface region probably due to beam induced disorder.

Angle-resolved XPS spectra of a 48 Å thermal and a 47 Å ion beam oxide are shown in Figure 5. XPS is performed using a non-monochromatized Mg-K_α source providing 1253.6 eV X-rays at a power of 240 W. The analyser is calibrated using the Au 4f7/2 peak with binding energy (BE) 83.8 eV. The calibration and the shifts due to substrate charging are checked throughout the runs by monitoring the C_{1s} peak (BE = 284.5 eV). Both the O_{1s} and Si_{2p} peaks were monitored with progressively shallower sampling depth as the detector was oriented progressively farther away from the surface normal. Figure 5(a) shows the presence of a sharp O_{1s} peak with BE = 533.1 eV at all detector angles which is evidence of the uniform stoichiometry of the thermally grown oxide film. The double Si_{2p} peak includes the silicon signal from the oxide layer (BE = 103.9 eV) and the substrate silicon signal (BE = 99.4 eV). The intensity of the substrate Si_{2p} peak decreases as the sampling depth decreases and disappears at $\theta = 70°$. The O_{1s} peak of the ion beam oxide, as shown in Figure 5(b) is much broader and comprises two unresolved components. The higher binding energy one (BE = 532.1 eV) dominates at $\theta = 0°$. The lower binding energy peak (BE = 531.6 eV) gradually increases in amplitude relative to the 532.1 eV peak with increasing detector angle and dominates at $\theta = 70°$. The behaviour of the lower BE component correlates well with the emergence and growth of a similar lower BE component of the oxide Si_{2p} at higher θ. These lower BE components suggest that the upper surface region consists of oxide with lower oxidation states than SiO_2 due either to the preferential sputtering of the lighter oxygen component or to the stopping depth of the impinging oxygen ions. The ion beam sample Si_{2p} oxide peak has BE = 102.9 eV, a typical value observed for very thin SiO_2 (ref 9).

The high electrical quality of the ion beam grown oxide films is best illustrated by the fabrication of n-channel MOS transistors with gate dielectrics formed by ion beam oxidation at room temperature. The current–voltage characteristics of such a transistor are shown in Figure 6. The gate has a 30 μm length and a 16 μm width. Leakage current through the gate is 6 nA at 1 V, however, this is several orders of magnitude lower than the drain-source saturation current at the voltages at which the transistor

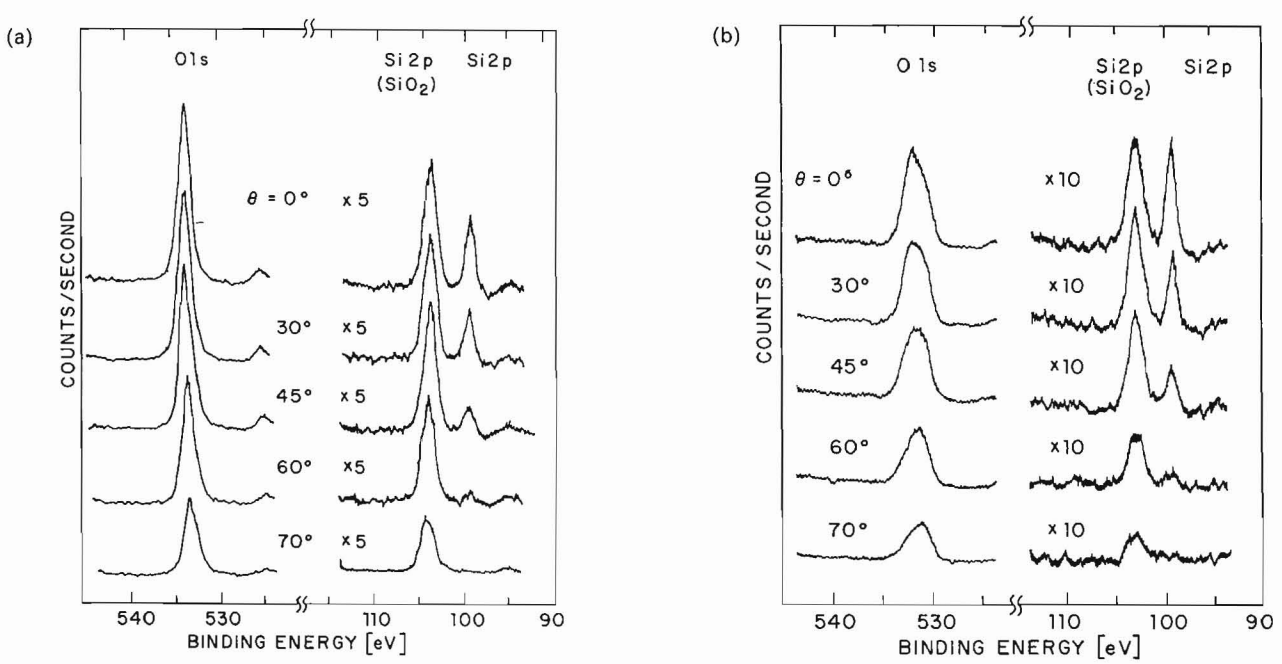

Figure 5. Angle-resolved XPS spectra of (a) thin thermal oxide and (b) thin ion beam oxide. θ is the angle between the surface normal and the detector.

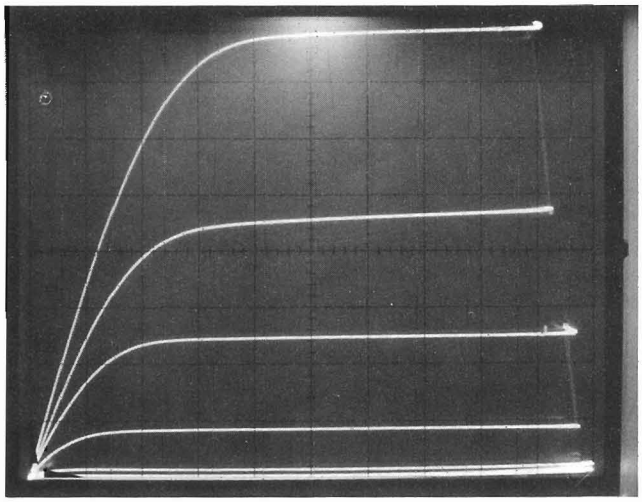

Figure 6. Current–voltage characteristics of a MOSFET fabricated by ion beam oxidation following post-metallization annealing: horiz.—0.2 V-/div; vert.—20 μA/div, 0.2 V/step. O_2 partial pressure: 6.5×10^{-5} torr. Ion energy: 60 eV. Time: 12 min.

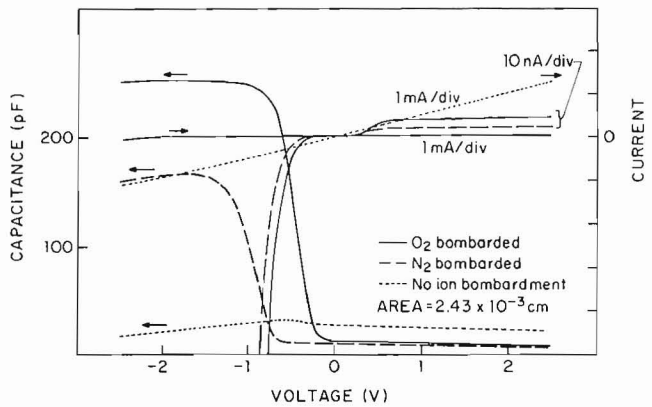

Figure 7. *C–V* and *I–V* characteristics of low energy ion beam oxide (solid curves), nitride (dashed curves), and control (dotted curves) MIS capacitors. 60 eV O_2 for 12 min at 6.5×10^{-5} torr. 80 eV N_2 for 6 min at 3.2×10^{-4} torr. Control sample at same conditions as oxide sample but with shutter closed.

operates and does not affect its successful operation. The breakdown strength of the oxide is at least 7×10^6 V cm^{-1}. The saturation mobility is calculated at 575 cm^2 (V s)$^{-1}$ making use of the value of the capacitance in accumulation.

It has been suggested that very thin silicon nitride films may be better dielectrics than silicon dioxide films of comparable thickness. In fact silicon oxynitride films have been successfully produced by 5 keV ion bombardment of silicon[10]. We have demonstrated the ability to produce nitride films on silicon at ion energies below 100 eV. Figure 7 presents a comparison of the *C–V* and *I–V* characteristics of aluminium gate MIS capacitors fabricated by low energy ion beams at room temperature. The control sample was fabricated by the same procedure except that it was not directly bombarded by the ions, since the shutter was not opened. The ohmic nature of the non-bombarded metal–silicon contact is expected and is evidence that not simply charged, but energetic species are necessary for the formation of the thin films. The figure also indicates that reverse-bias leakage current of the nitride sample is lower than that of the oxide by a factor of two.

Summary

Device-quality ultra-thin dielectric films have been produced on silicon substrates bombarded by reactive ions with energies 60–80 eV. The damage induced by the ion beam does not significantly affect device operation.

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