

Oxidation of silicon by a low-energy ion beam: Experiment and model

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The self-limiting oxidation of silicon by a low-energy ion beam (40–120 eV) is described by an implantation-sputtering model. The thin oxide (40–50 Å) is grown primarily by a surface implantation process which leads to a logarithmic increase of oxide thickness with dose in the absence of sputtering. At higher energies (100 eV), the sputtering of the growing film leads to net self-limiting growth. The model, which does not include adjustable parameters, is used to describe the dose evolution of the oxide growth as a function of beam energy. The implantation-sputtering model is found to be in excellent agreement with experimental observations.

The room-temperature oxidation of silicon by the use of a broad, low-energy ion beam containing a mixture of argon and oxygen has been shown to produce an oxide suitable for use as a gate dielectric in metal-oxide-semiconductor (MOS) transistors.^{1,2} The ion beam energy is typically in the range of 40–120 eV with doses of the order $10^{17}/\text{cm}^2$ delivered in 3–5 min, leading to oxides of thickness 40–50 Å. The oxides are found to be stoichiometric SiO_2 as measured by Auger electron spectroscopy and x-ray photoelectron spectroscopy. The thickness of the films is measured after growth using several techniques, the primary one being ellipsometry.³ The film thickness has a weak dependence on substrate temperature in the range 25–650 °C, on dose, and beam energy.⁴ The oxide thickness uniformity as measured by test sites across a wafer is excellent and far exceeds the dose uniformity. This letter presents an implantation-sputtering model to describe the oxidation process. The model predictions are in excellent agreement with the above experimental observations.

In the implantation-sputtering (I-S) model, the oxide growth is governed by a surface implantation process, rather than by thermal diffusion. This is in contrast to a previous model suggested for the low-energy ion beam oxidation of metals⁵ and is supported by the weak dependence on substrate temperature. The range distribution of the oxygen ions in the target is calculated using linear cascade theory.^{6,7} Energy loss occurs entirely by elastic binary collisions with the target nuclei. The target is treated as homogeneous, isotropic, and monatomic with target-atom mass and atomic number determined according to Bragg's rule and taking into account the gradual transformation of the target from silicon to silicon dioxide. The interatomic potential used is the universal potential.⁸ Power-potential approximations⁷ obtained by a least-squares fit to this potential are used to allow analytical solution. Thus, $m = 1/5$ is used to fit the potential at reduced energy in the range 10^{-5} – 2×10^{-3} . The mean and the straggling of the distribution are calculated and it is fitted by a simple Gaussian. The results of this calculation in the case of 50 eV O^+ bombardment of SiO_2 are presented in Fig. 1. This corresponds to the case of 100 eV O_2 ion beam bombardment. It should be noted that while the mean range

is predictably small (approximately 5 Å) the straggling is significant. It is this straggling tail which governs the oxide growth evolution.

In the I-S model, the oxide growth competes with the simultaneous sputtering of the oxide film by the same beam. Since the experiments are primarily performed with 50%-50% argon-oxygen mixtures, the sputtering of the target is due mainly to the argon bombardment. The sputtering rate of SiO_2 under low-energy argon ion bombardment has been measured in a separate set of experiments⁹ and the results are shown in Fig. 2. Sputtering at 60 eV can be considered negligible for the oxide thicknesses considered, but becomes appreciable by 100 eV.

A computer simulation of the oxide growth evolution has been performed using the I-S model. The incorporation of oxygen into the target and the conversion of Si to SiO_2 is accompanied by volume expansion. To account for this, the evolution of the oxide layer is calculated in small (oxygen dose) time increments. The range distribution is recalculated for each time interval. It is assumed that the implanted oxygen reacts immediately with unreacted silicon, since the former may be considered "hot" in the last stages of stopping. However, oxygen coming to rest within stoichiometric SiO_2 is assumed to outdiffuse to the surface. In thicker oxides, consideration of a spatially dependent diffusion coefficient may become necessary in view of the depth dependence

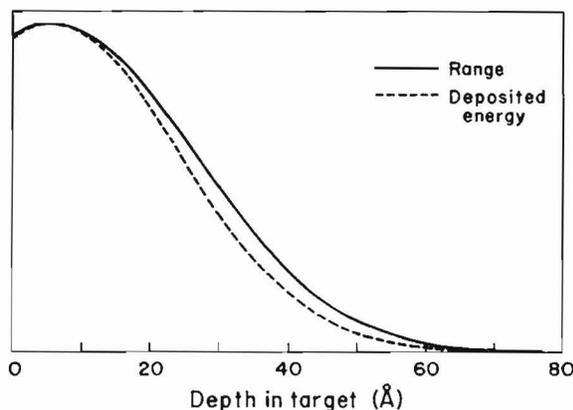


FIG. 1. Normalized range and deposited energy distributions calculated for 50 eV O^+ on SiO_2 .

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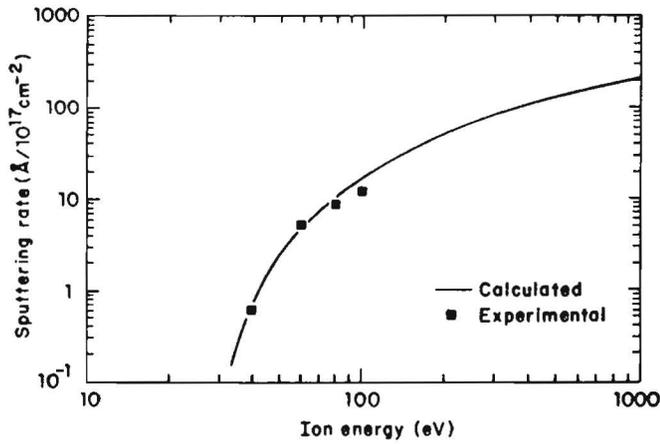


FIG. 2. Sputtering rate for low-energy argon ion bombardment of silicon dioxide. Rate is measured in angstroms sputtered per dose of 10^{17} incident ions per cm^2 .

of the beam energy deposition and consequent defect production.

The stoichiometry of the film as a function of depth for increasing dose is shown in Fig. 3 for the case of 100 eV O_2 bombardment. An interesting feature of the evolution is apparent. It is seen that the interface between oxide and silicon is initially broad, but as the surface erodes due to sputtering, the interface becomes more sharp. The width of the interface explains electrical characterization results, such as lower channel mobility in ion beam oxide MOS transistors, and anomalously larger capacitance-voltage measurements of oxide thickness.¹⁰

The simulated dependence of the oxide film thickness on ion dose for 100 eV bombardment is presented in Fig. 4, where it is compared to experimental results. Since the experimental data are obtained by ellipsometry, the simulated thickness is determined in two ways. In the low dose case, where no stoichiometric oxide has been formed, the thickness is plotted according to the position of the steepest gradient in oxygen concentration, which is approximately halfway through the transition region. For higher doses, in which stoichiometric SiO_2 has been formed, the edge of the stoi-

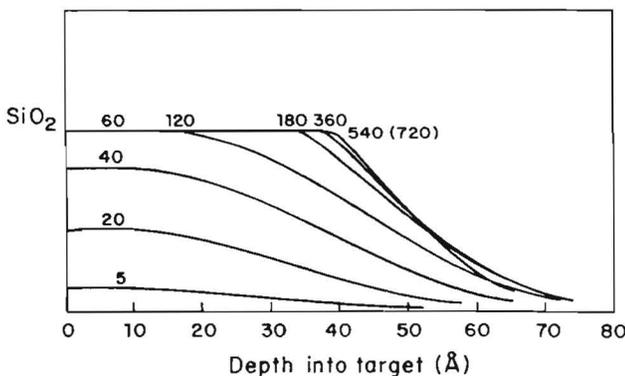


FIG. 3. Simulation of oxide growth evolution. Plot shows bonded oxygen concentration as a function of depth for 100 eV O_2^+ ion bombardment. Numbers indicate elapsed time in seconds for an ion beam current density of $100 \mu\text{A}/\text{cm}^2$.

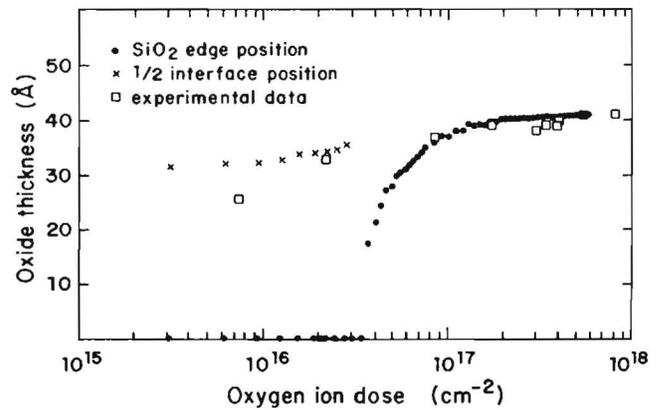


FIG. 4. Oxide thickness as a function of dose measured experimentally and simulated using the implantation-sputtering model for 100 eV O_2^+ bombardment.

chiometric region is used to assess the thickness. For 60 eV bombardment simulations in which sputtering is negligible, the film thickness grows logarithmically with dose, and is also in excellent agreement with experimental observations.

The simulated final oxide thickness as a function of ion beam energy is shown in Fig. 5. Also shown are the experimental data, which show good agreement. Note that the experimental and simulated data show a maximum in thickness for the 50–60 eV energy range. The maximum is a result of the competing processes of implantation and sputtering. The calculated thickness for 140 eV bombardment is lower than the experimental data due to an overestimation of sputtering in the I-S model. The low-energy ion beam sputtering model of oxides assumes that sputtering of oxygen is not rate limiting, an assumption which begins to fail at higher energies.⁹

In summary, an implantation-sputtering model without adjustable parameters has been presented for the low-energy ion beam oxidation of silicon. The model explains the weak dependence of oxide thickness on temperature, energy, and dose. The excellent agreement between simulation and experiment allows the important conclusion that range and straggle predicted by linear cascade theory and the binary

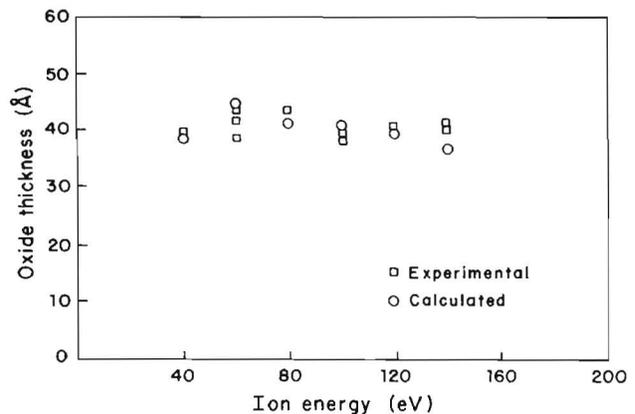


FIG. 5. Oxide thickness as a function of ion energy measured experimentally and simulated using the implantation-sputtering model. O_2 dose: $3 \times 10^{17} \text{ cm}^{-2}$.

collision approximation appear to be applicable at these low ion energies.

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