

THIN OXIDE GROWTH USING LOW ENERGY ION BEAM BOMBARDMENT

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ABSTRACT

Bombardment of silicon surfaces by low energy oxygen ions has been studied as a possible process for growing films of SiO₂ at room temperature. Broad ion beams of energy 40-200 eV and variable oxygen content have been used to grow ultra-thin oxides of extremely uniform thickness. The dependence of the thickness and quality of the oxide films on ion dose, ion energy and substrate temperature have been investigated. The obtained thickness varies only slightly with increasing substrate temperature up to 650°C which indicates a non-thermally driven process. The ion-beam oxides quickly reach a thickness of 40-60 Å, after which they are largely insensitive to ion dose. The oxide thickness is also found not to depend on ion energy in this energy range.

The limited thicknesses are explained by the enhancement of the mobility of the oxygen atoms in the target only at the depths which are currently being reached by the beam. As the oxide film thickness grows the oxide-semiconductor interface moves beyond the ion penetration depth and the oxidation effectively stops. Thus, limited thicknesses are expected even if target sputtering is negligible.

INTRODUCTION

Future development of high density integrated circuits (ICs) places stringent requirements on the control over the device dimensions and will require reduced temperature processing during fabrication. The trend toward larger substrates places the additional requirement of good control over the lateral uniformity of the gate oxides in MOS applications. Thus, the problem of obtaining high quality thin films of SiO₂ at reduced temperatures has a special significance. Various techniques have been proposed as alternatives to thermal oxidation for production of gate dielectrics for MOS devices at lower substrate temperatures. Among these are plasma oxidation at 500-600°C [1,2] and rf sputtering at 200-300°C [3]. Very thin SiO₂ films of high electrical quality have also been deposited by plasma enhanced chemical vapor deposition (PE-CVD) at 350°C [4]. MOS transistors have been fabricated using very thin gate dielectrics grown at 25°C by ion beam oxidation [5].

The electrical characteristics and other properties of the very thin oxide films grown at room temperature by ion beam oxidation have been reported previously [5,6]. Briefly, these showed that ion beam oxides are similar to thermally grown SiO₂ films of equal thickness in many respects. They have almost identical Auger sputter profiles except for the apparently sharper interface of the thermal oxide. X-ray photoelectron spectroscopy at glancing detector angles

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indicated the presence of lower oxides of silicon at the film surface. The most notable difference between thermal and ion beam oxides is the 2-3 orders of magnitude greater leakage current in reverse bias for the latter. However, this leakage is another three orders of magnitude lower than the drain-source saturation current and thus did not degrade MOSFET performance [5]. This paper will concentrate on the dependence of the oxide growth kinetics on the ion bombardment conditions and will propose a mechanism to explain the oxidation behavior.

EXPERIMENTAL DETAILS

Thin films of silicon dioxide are grown on device grade (100) silicon wafers, 5-cm diameter, polished on one side. Both p-type and n-type wafers of resistivity 2-5 $\Omega\cdot\text{cm}$ are used. The samples are cleaned in chemical baths. Two thick 900°C oxides are sequentially grown in steam and stripped after which the wafers are loaded into the ion beam processing chamber. The wafers are mounted on a temperature-controlled copper substrate holder positioned 15 cm below the extraction grid of the ion source. Ion beam oxidation is performed using a single-grid broad-beam ion source, described previously [6]. The source operates on a mixture of argon and oxygen. The addition of argon buffer gas is necessary to improve the stability of the source over extended periods of time. The base pressure in the ion beam processing chamber is 2.5×10^{-7} mbar; the operating pressure is 5×10^{-7} mbar. The thickness of the obtained films is measured with a He-Ne laser ellipsometer after unloading the wafers from the ion beam machine. These measurements correlate well with values obtained by Auger sputter profiling, calculated from the ratio of the XPS Si 2p peaks or calculated from the capacitance-voltage characteristics of MOS capacitors [6,7].

RESULTS AND DISCUSSION

The dependence of the obtained ion beam oxide thickness on oxygen ion dose is presented in Fig. 1. The silicon wafers were bombarded by a 60 eV ion beam containing O_2 and Ar in a 1:1 ratio. The substrate temperature was monitored by a substrate-holder mounted thermocouple and is 25°C. The figure shows that there is an approximate logarithmic dependence on the oxygen ion dose, though the scatter in the data is more pronounced at higher doses. This scatter is associated with instabilities in the operation of the ion source which are more prominent at the longer exposure times necessary to achieve higher doses. It appears that the n-type wafers oxidize somewhat more slowly than the p-type wafers; however, the differences are within the experimental uncertainty. It has been observed previously that the ion beam oxides exhibit very good thickness uniformity over the surface of the wafer even though they are grown by an ion beam which has a peaked gaussian-like profile [5]. This effect was attributed to the attaining of a self-limiting value of the thickness. While it is now evident that a self-limiting thickness has not yet been reached, it is also clear that the growth rate becomes sufficiently low at high doses so that such increases in the ion dose would not lead to noticeable changes in the oxide thickness.

Self-limiting oxide growth has been observed in the case of rf oxidation of lead [8] and ion beam oxidation of nickel [9]. It is attributed to the achieved balance between the competing processes of oxidation and sputtering. The oxidation rate is assumed to decrease with increasing film thickness whereas the sputtering rate remains constant. Thus the oxide growth will stop at a thickness value at

which the two rates become equal.

It is expected that self-limitation will occur earlier at higher ion beam energies where sputtering is more pronounced. That is

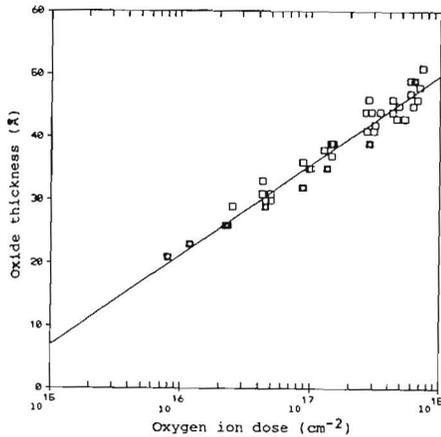


Fig. 1. Ion beam oxide thickness as a function of oxygen dose. Ion energy: 60 eV. □ - p-type silicon; ■ - n-type silicon.

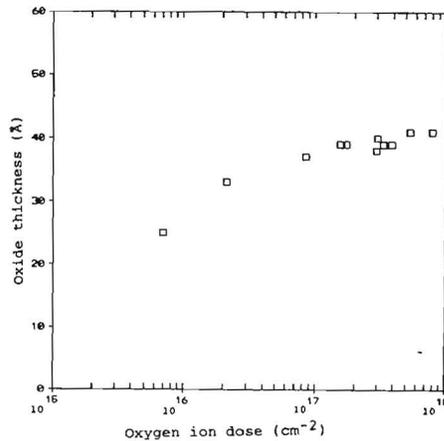


Fig. 2. Ion beam oxide thickness as a function of oxygen dose. Ion energy: 100 eV.

indeed the case as shown in Fig. 2. The samples are bombarded with a 100 eV ion beam with a 1:1 $O_2:Ar$ ratio at $25^\circ C$. A comparison with the 60 eV data indicates that higher initial oxidation rates are observed at the higher ion energy. This is probably related to the increased incorporation probability associated with the larger penetration depth. The oxidation rate then decreases more quickly than for 60 eV ions and appears to exhibit self-limiting behavior.

The importance of beam heating of the substrate during ion bombardment was investigated by oxidizing several samples at different ion dose rates leading to the same received dose. No differences in the properties of the obtained oxides were observed.

The substrate may be intentionally heated up to $650^\circ C$ by means of resistive heating of the substrate holder. The obtained oxide thickness for fixed ion beam conditions is observed to increase with increasing substrate temperature. However, this dependence is rather weak, especially considering the large temperature range. An Arrhenius plot of this data, shown in Fig. 3, allows the extraction of an activation energy E_{act} for the process. The oxidation rate dependence has been approximated by $x = C \ln t$, where t is the oxidation time and C is a constant which is assumed to depend on the temperature T in the standard fashion: $C = C_0 \exp(-E_{act}/kT)$, where k is the Boltzmann constant. Note that the data is largely independent of ion dose. The slope of the obtained straight line allows the determination of $E_{act} = 7$ meV. For comparison, the activation energy of the linear rate constant B/A defined in thermal oxidation of silicon is 2 eV [10]. Clearly, oxidation due to ion bombardment relies on non-thermal mechanisms of enhancing the diffusivity and reactivity of the oxidizing species.

The observed oxide thicknesses correlate well with the expected oxygen ion projected range, accounting for the volume expansion which accompanies the conversion of silicon to SiO_2 . Thus, the obtained thickness may be expected to increase at higher ion energies. The

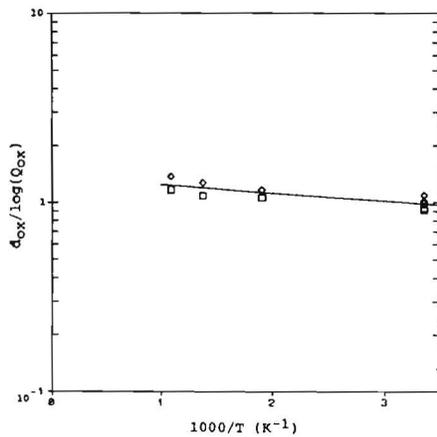


Fig. 3. Arrhenius plot for ion beam oxidation. \square - O dose: $1.3 \times 10^{17} \text{ cm}^{-2}$. \diamond - O dose: $2.7 \times 10^{17} \text{ cm}^{-2}$.

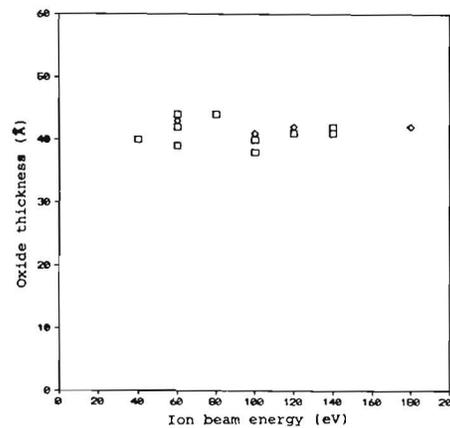


Fig. 4. Ion beam oxide thickness as a function of ion energy. \square - O dose: $1.3 \times 10^{17} \text{ cm}^{-2}$. \diamond - O dose: $3.0 \times 10^{17} \text{ cm}^{-2}$. \circ - O dose: $5.3 \times 10^{17} \text{ cm}^{-2}$.

dependence of oxide thickness on ion energy for a fixed oxygen ion dose is shown in Fig. 4 for beams with a 50% oxygen content. The lack of a trend over the covered energy range is evident. This is an indication that the same mechanism governs both the oxidation process and the sputtering processes.

A series of experiments were performed to investigate the importance of sputtering in this process. Calculations indicate that most of the sputtering that accompanies the oxidation process is due to the argon bombardment. Therefore, it was considered appropriate to measure the sputtering yield for Ar on SiO_2 at energies below 100 eV. The thickness of dry thermal oxides grown at 900°C was measured by ellipsometry before and after sputtering. The change in thickness was plotted versus the ion dose and the sputtering rate per 10^{17} Ar ions was obtained from the slope of this plot. These results are presented in Fig. 5 together with experimental data of Jorgenson and Wehner [11]. The measured sputtering rates are compared to various calculated predictions [12-14]. The SiO_2 sputtering rate was calculated using the respective standard values for sputtering of Si with an assumed density equal to half of the silicon number density. This is an attempt to describe the sputtering of SiO_2 by the rate-limiting process of sputtering the silicon component from a less dense matrix. Indeed, a metal enrichment of the surface layer has been observed for sub-keV inert-gas bombardment of oxide targets [15]. The agreement between the data and the calculation is surprisingly good.

This data indicates that sputtering is unimportant at 60 eV but plays a role at 100 eV. The expected eroded thicknesses for typical exposures to the beam in these cases is 4 Å and 13 Å, respectively.

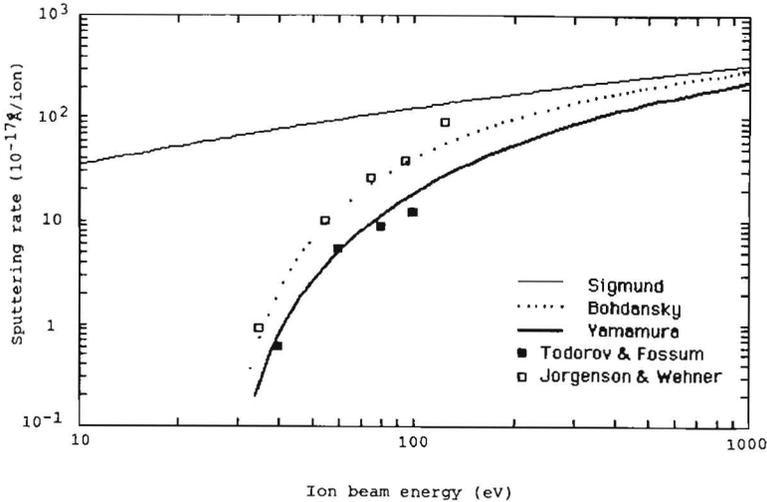


Fig.5. Sputtering rate for Ar on SiO₂.

PROCESS MODEL

Models of low energy ion beam oxidation of metals describe the oxidation process in the absence of sputtering as decreasing exponentially with increasing exposure time [9]. However, this model is carried over from the process of rf oxidation of metals in which a self-biasing of the oxide layer is observed [8,16] and does not account for the fact that the oxidizing species are actually deposited below the surface. Also it does not explain the observed enhancement in the oxidation rates over thermal oxidation processes. The thin oxide can pass sufficient current to avoid charging of the surface.

Low-energy ion beam oxidation of silicon is treated here as a scaled-down version of the high-energy high-dose oxygen implantation processes used for obtaining buried layers of SiO₂ in silicon-on-insulator (SOI) technology. The models developed to describe this process introduce an enhanced effective diffusion constant and reaction rate and also take into account the swelling of the target [17,18]. These models, however, neglect any spatial dependence of the enhancement. This leads to the prediction of preferential growth toward the substrate [14] whereas it has been observed that the growth of the buried oxide layer takes place mostly at the top interface [19,20]. The preferred oxidation upwards has been attributed to the presence of silicon interstitials at the lower Si-SiO₂ interface [21] which cannot recombine due to the very large distance to the back surface of the wafer.

We propose an important modification to these models. While it is clear that sputtering plays an important role at higher energies, the explanation of enhanced oxidation in unheated substrates is considered unsatisfactory. It is proposed that the enhanced reactivity and mobility of the oxidizing species are due to the energy being deposited by the ion beam. Thus, at any time, oxidation is taking place only at those depths which are currently being reached by the ion beam. In other words, it is important to recognize that the effective process rates are spatially dependent.

Because of the volume expansion which accompanies the conversion of silicon to silicon dioxide this spatial dependence means translates into a time dependent oxidation rate at the oxide-semiconductor interface. Oxidation at the lower interface will stop when a sufficient portion of the substrate has been converted to SiO_2 and the accompanying swelling effectively prevents later ion arrivals from reaching the SiO_2 -Si interface. The non-bonded oxygen atoms will move freely in the SiO_2 layer due to the enhanced-diffusion effect; however, this diffusion will be preferentially outward. Note that the concept of a temperature increase due to thermal spikes or beam heating is not necessary for this treatment. Enhanced mobility and reactivity may be due to other beam related processes like the creation of excess numbers of defects in the vicinity of an atom, the transfer of excess energy to the atom in a collision [22] or the excess energy of the not fully thermalized ion itself.

This model accounts for the enhanced oxidation rates observed for unheated substrates under ion bombardment and the insensitivity to substrate temperature observed in experiments on low energy ion beam oxidation of silicon. Further, it naturally explains the limited thicknesses observed with this technique even in the absence of sputtering. The model is simply extended to the production of buried oxides by high energy oxygen implantation and is in qualitative agreement with the observed preferred growth toward the top surface of the wafer. A quantitative evaluation of the process parameters based on this model will be published separately.

CONCLUSION

The bombardment of silicon surfaces by low energy oxygen ion beams leads to the growth of ultra thin films of silicon dioxide. The oxide thickness is limited and very uniform. Limited thicknesses are also observed in the absence of sputtering. The oxidation process is explained in terms of beam-enhanced reactivity and mobility of the oxidizing species. The importance of recognizing the spatial limitations of the enhanced oxidation process is stressed. The explanation of the process is extended to buried SiO_2 layers produced by oxygen implantation.

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