

Sputtering of silicon dioxide near threshold

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The sputtering rate for silicon dioxide by argon ion bombardment at energies appropriate for ion beam deposition (< 100 eV) has been measured. It has been found that the energy dependence of the oxide sputtering rate at these low energies is easily predicted by assuming the yield is limited by the metallic component of the binary target. This assumption is shown to predict also the sputtering rate of other metallic oxides.

Bombardment of growing thin films by low-energy ion beams has evolved into an important technique for the modification and deposition of thin films. Ion beam etching and reactive ion etching have achieved widespread application. More recently, the use of lower ion energies has led to the development of direct ion beam deposition applied to low-temperature epitaxial growth of Si and Ge.¹⁻³ Oxygen and nitrogen ion beams have been used for the controlled growth of ultrathin oxide and nitride films on metal and semiconductor substrates.⁴⁻⁷

These techniques allow good control over the composition, stoichiometry, orientation, and crystallinity of the obtained films. The basic factor that limits the film growth rate in ion beam deposition is the sputtering due to the ion bombardment. The growth rate can be approximated by $dx/dt = (1/N)(\eta\Phi - Y\Phi)$, where N is the density of the material, η is the sticking coefficient or incorporation probability, Y is the sputtering yield, and Φ is the ion flux. For deposition to take place, it is necessary that $Y < \eta$. In the case of the ion beam oxidation, it has been observed that a limiting oxide film thickness is reached which is related to the sputtering rate of the material.^{4,7} It is evident that sputtering plays an important role in film growth by direct ion bombardment.

In this letter we report experimental results of sputtering of SiO₂ by Ar ions at energies below 100 eV. Accurate knowledge of the sputtering rate and its energy dependence at these low energies is becoming increasingly important in microelectronics device fabrication processes. The use of inert-ion bombardment precludes film growth and allows separate investigation of the sputtering component of the deposition process. It is shown that a simple assumption leads to good agreement between existing theory for nonbinary materials and the reported measurements, not only for the case of silicon dioxide, but also for other oxide targets.

The experiments are performed on samples prepared by oxidizing chemically cleaned *p*- and *n*-type Si (100) wafers in dry oxygen at 900 °C for times ranging between 10 min and 3 h, and resulting oxide thicknesses of 45–520 Å. The thickness of the oxide films is measured with a He-Ne laser ellipsometer immediately before loading them into the ion beam processing chamber. The samples are mounted 15 cm from the ion source in a vacuum chamber with a base pres-

sure of 2×10^{-7} Torr. Broad Ar⁺ ion beams with energies in the range 40–100 eV are produced by a single-grid Kaufman ion source. The SiO₂ samples are bombarded with argon doses ranging from 1×10^{17} to 1.6×10^{18} cm⁻². The thickness of the remaining oxide is remeasured by ellipsometry after the samples are unloaded from the vacuum system. The accuracy of the ellipsometric data is approximately 1 Å, and although it may be distorted by damage to the substrate,⁸ this is not expected to be significant in this case. For example, measurements on substrates in which the oxide has been completely sputtered away indicate a “residual” film thickness of 3–5 Å, attributable to a monolayer of native oxide grown after the substrate is removed from the vacuum system.

The measured change in oxide thickness is plotted as a function of the ion dose for each value of ion energy. Six to ten different data points are plotted for each energy, and the value of the sputtering yield is determined from the slope of the least-squares fit through the data points. The data for the case of 60 eV Ar⁺ bombardment are shown in Fig. 1. The thickness decrease with increasing ion dose is linear and independent of the initial oxide thickness.

The measurement of the sputtering rates at energies close to the sputtering threshold is difficult to measure because of the relatively low yields involved. For example, Oostra *et al.*⁹ did not observe any sputtering of SiO₂ at argon energies less than 50 eV when examining scanning electron micrographs. It is believed that the method used here allows

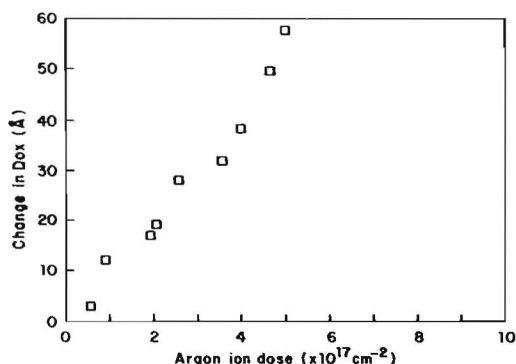


FIG. 1. Measured decrease in the thickness of the SiO₂ film as a function of Ar dose. $E = 60$ eV and Ar⁺ flux = 2.2×10^{15} cm⁻² s⁻¹.

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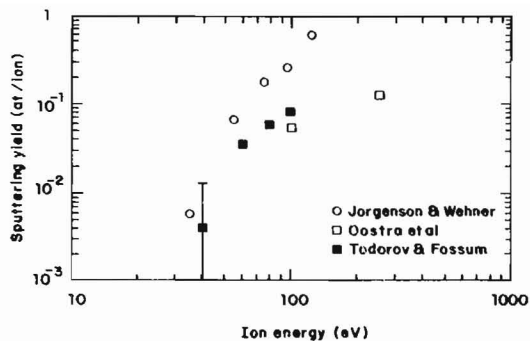


FIG. 2. Experimental results on sputtering of silicon dioxide by low-energy argon ions.

significantly more precise measurement of the sputtering rate, and material removal has been observed at energies as low as 40 eV.

The experimental results on sputtering SiO_2 by Ar ions are summarized in Fig. 2, where they are compared to the experimental data of Jorgenson and Wehner¹⁰ and the higher energy data of Oostra *et al.*⁹ Note that although widely cited, the data of Jorgenson and Wehner are obtained under quite different experimental conditions with the oxide film covering a thin tungsten wire immersed in a dc discharge.

Theoretically, the sputtering of monatomic targets is well understood,¹¹ and good descriptions of the sputtering yield near thresholds can be obtained by semiempirical formulas¹²⁻¹⁴ that introduce modifications of Sigmund's theory to account for the existence of a sputtering threshold. Very good agreement with experimental data is generally observed.

The sputtering process for multicomponent targets is more difficult to describe. The collision cascade process will affect each target component differently. Apart from causing the ejection of atoms from the target surface, the ion bombardment may also lead to target mixing, segregation, enhanced diffusion, and other processes.¹⁵ Thus the correct description must take into account the changes in composition of the target brought about by the ion bombardment and how these changes are reflected in the sputter particle flux. This discussion will concern only the sputtering of oxides; the behavior of compounds or alloys consisting only of low-vapor-pressure materials may be quite different.¹⁶

In this letter the simple assumption is made that oxygen is initially preferentially ejected and that the nonvolatile component (silicon) limits the sputtering process. This assumption is supported by prior experimental evidence that the sputtering of metallic oxides by low-energy (< 1 keV) ions leads to the enrichment of the metal component within several monolayers of the surface.¹⁶ This effect is expected to become especially pronounced at energies near the metal sputtering threshold, in agreement with the general observations on sputtering of binary targets whose components have different sputtering threshold energies.¹⁵

Further support for this assumption comes from previously reported experimental data concerning the sputtering yield of Ta and Ta_2O_5 .¹⁷⁻²⁰ Our assumption correctly predicts that the removal of equal numbers of tantalum

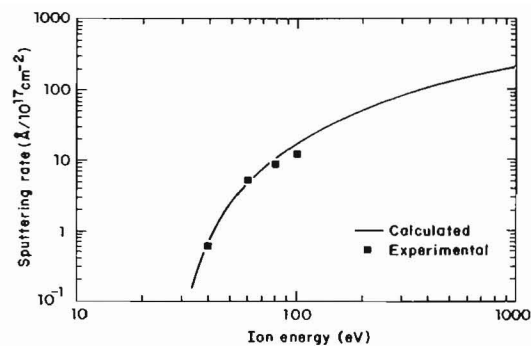


FIG. 3. Comparison of calculated and measured sputtering rates for Ar^+ -bombarded SiO_2 .

atoms leads to a 2.48-fold decrease in the volume of Ta_2O_5 , as compared to Ta, for 100 eV Ar^+ and 500 eV He^+ bombardment. This ratio degrades with higher bombardment energies, since the ejection of the material takes place from a layer whose composition can no longer be approximated as pure tantalum.

Applying this assumption to the case of low-energy argon sputtering of silicon dioxide leads to the similarly correct predictions. The removal of the same number of silicon atoms will decrease the volume of a SiO_2 sample 2.21 times the change in the volume of a silicon sample. Thus use of the sputtering yield of silicon calculated according to Matsunami *et al.*¹³ with the threshold energy $E_{\text{th}} = 27$ eV as suggested by Yamamura and Bohdansky¹⁴ leads to excellent agreement with the experimentally obtained data, as shown in Fig. 3. The inadequacy of the assumption at higher energies is pointed to by the slight deviation of the data from the predicted curve.

In summary, the sputtering yield of SiO_2 under low-energy argon ion bombardment has been measured in the range 40–100 eV. An assumption for understanding the energy dependence in terms of low-energy silicon sputtering with a simple volumetric rate adjustment leads to excellent prediction of the experimental data. The assumption has been extended to predicting other oxide sputtering rates with equal success.

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