II. NOVEL OXIDATION METHODS AND CHARACTERIZATION

INTRODUCTION

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The trend to lower processing temperatures in the fabrication of high density ULSI devices has encouraged the development of enhanced thermal oxidation procedures. These have included chemical, electrical, physical, and optical excitation methods. Such excitation can result in modifications of physical as well as electrical properties of the resulting oxides, in addition to effects on the oxidation kinetics. Several examples of enhanced oxidation are described in the first half of this chapter.

R. J. Jaccodine reviews the chemically enhanced thermal oxidation by chloride and fluorine compounds. The most striking results are the following: 1) some ppm of fluorine compounds (NF3, C2H3C12F) in the O2 gas induce a significant increase of the oxide growth rate (a factor of 10 at 1000°C for 500 ppm), 2) a very fast shrinkage of already grown stacking faults occurs during O2/NF3 oxidation. This indicates that the basic difference between this process and classical oxidation is the creation of a vacancy-rich interface.

J. Joseph, Y. Z. Hu and E. A. Irene present an in-situ spectroscopic ellipsometry study of the electron cyclotron resonance (ECR) plasma oxidation of silicon and interfacial damage. The ECR source was operating at 300 W, 2.45 GHz with an oxygen pressure of 4 \times 10^{-4} Torr at oxidation temperatures between 80 and 400°C. Accelerated growth under positive
substrate bias indicates that a negative atomic species dominates the growth above an oxide thickness of 4 nm. Kinetics results are compatible with the Cabrera-Mott theory, however this assumption needs to be checked. The damage layer appears to be composed of SiO₂ with amorphous Si and due to the oxidation reaction at low temperature (<500°C) rather than the ions from the plasma.

L. M. Landsberger discusses the mechanisms of oxidation rate enhancement in negative-point oxygen discharge at atmospheric O₂ pressure and 600-900°C while creating SiO₂ relaxed films. A simple model is developed and includes the effect of relaxation of oxide by O⁻ ions, enhanced oxygen diffusion, and O⁻ flux. Reactions and atomic transport mechanisms in the oxide corresponding to the O⁻ flux remain debated questions.

Conventional oxidation at high temperature of Si₁₋ₓGeₓ produces oxides which, due to the segregation of Ge at the oxide/substrate interface, are useless to device applications. C. Caragianis, Y. Shigesato, and D. C. Paine show that oxidation at very high pressure (500-700 atm) allows the growth of oxide at low temperatures (550°C). This produces high quality oxide which incorporates Ge into the oxide.

The above results all tend to indicate that enhanced thermal oxidation at reduced temperature may be beneficial for future fabrication of advanced device structures. In addition, such techniques can help provide a valuable insight into mechanisms of thermal oxidation.

An important aspect of developing new methods of oxidation is that of characterization of the silicon surface and the oxidized silicon structure. In the second part of this chapter, several methods of such characterization are reported. These include spectrographic ellipsometry of thermally oxidized silicon by E. A. Irene and V. A. Yakovlav; infrared spectroscopy of low temperature plasma deposited oxides over thermal oxides by S. Fujimura and co-workers; infrared spectroscopy and ellipsometry of both thermal oxides and remote plasma deposited oxides by C. E. Shearon and co-workers; and transmission electron microscopy (TEM) of thermally oxidized amorphous silicon by M. Reiche. In investigations involving optical methods of analysis, some differences of opinion exist regarding interpretation of results. Therefore, various conclusions have been reached regarding properties of oxide-silicon interfaces. Undoubtedly, more experiments and data will be forthcoming to provide a better understanding of Si-SiO₂ interface structure. Other analysis tools, such as scanning tunneling microscopy and its offspring, may help in this respect as well.