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An In-Situ Spectroscopic Ellipsometry Study Of The Electron Cyclotron Resonance Plasma Oxidation Of Silicon And Interfacial

by

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Damage

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Abstract

The growth of SiO, films on Si and the evolution of interfacial damage resulting from electron cyclotron resonance plasma oxidation studied in-situ during process spectroscopic was using ellipsometry. Accelerated growth under positive substrate bias indicates that negative atomic species dominate the growth above an oxide thickness of 4 nm. Below this thickness bias appears less important. The interfacial damage is different in both nature and extent from that caused by ions with higher energies. It appears that the damage layer is composed of SiO_2 with a-Si and is due to the oxidation reaction rather than the ions from the plasma.

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The use of plasmas to grow SiO, films on Si for electronic applications dates to the beginning of the Si technology¹. However successful these early workers were at producing oxide films, the electronic quality of the films and particularly the Si-SiO, interface was not adequate for device applications. More recent attempts²⁴ were far more successful at attacking the interfacial quality issue, but the best processes usually included elevated temperatures in oxygen either before or during plasma treatment or both. Recent research on plasma processing shifted to producing chemically vapor deposited, CVD, oxides of nearly the same quality as produced by thermal oxidation with the use of both local and remote plasma techniques configured to reduce interface damage⁵⁻⁷. Considerable research underlies the belief that the energetic plasma and/or ion beam processes produce substrate damage concurrently with film formation²⁻³. We (and many others) have used in-situ during process, ISDP, spectroscopic ellipsometry, SE, to study the production of damage along with surface cleaning, film etching and film growth.

The present study uses ISDP SE in the electron cyclotron resonance, ECR, oxygen plasma environment to investigate the early stages of plasma oxidation of Si. We report conditions which enhance the plasma growth, minimize Si damage and yield information relative to the plasma oxidation mechanism. X-ray photoelectron spectroscopy, XPS, was also performed to confirm the SE results. We report that the damage measured by SE analysis is located on the oxide side of the Si-SiO₂ interface and due to the oxidation

reaction at the $Si-SiO_2$ interface. This damage is decidedly different in nature than the crystallographic damage seen with ion beam processing.

Plasma oxidation was performed on high resistivity Si wafers that were cleaned⁹ and placed in a vacuum chamber equipped with a homemade ECR plasma source and high precision automated spectroscopic ellipsometer. The system with SE characteristics and alignment procedures were previously described^{10,11} and applied to ion beam studies. The plasma conditions were: 300W, oxygen pressure of 5×10^4 torr which resulted in a sample temperature during oxidation of about 80°C. The results that follow were made with the sample normal to the plasma and with sample biases of 0V, +30V and -30V. The bias conditions were chosen to be above the +17V plasma potential. The sample would be negative with respect to the plasma at both 0V and -30V, and positive only at +30V applied sample bias.

Fig. 1a shows a typical pseudo-dielectric function, $\langle \epsilon \rangle$, set of spectra as obtained from SE, in terms of both ϵ_1 and ϵ_2 versus photon energy, as a function of oxygen plasma exposure time, the oxidation time, for normal incidence of the plasma source with the sample surface, and with an applied substrate bias of 0V. Fig. 1a is representative in that no new spectral features were observed under the other experimental conditions, and the data are analyzed (below) using a best fit optical model in terms of oxide and damage layer thicknesses. In order to analyze the measured $\langle \epsilon \rangle$ data, we use the Bruggeman effective medium approximation, BEMA, with two discrete but compositionally inhomogeneous films. We do not

exhaustively justify this approach here, but there exists considerable work both in our laboratory¹⁰⁻¹² and elsewhere¹³⁻¹⁶ where this model has been found to yield excellent results that are concordant with both the SE results and independent measurements of the SE obtained parameters. In this model film 1 is the top layer which in our case is the plasma grown oxide, and film 2 is the damaged layer in between the pure SiO₂ and the c-Si substrate. Film 2 has been found from the present BEMA analysis to be composed of SiO, and a-Si. In the course of the present research we have assumed that film 1 can also be damaged and we used fractions of a-Si to represent the damage; we have also assumed that a damaged layer exists both above and below film 1; and we have tried models where one or both of the above mentioned components of film 2 are absent as well as also containing fractions of c-Si and voids. The results show that the best fits were consistently obtained using the model shown in the inset of Fig.1b which indicates a pure SiO, film, film 1, on a damaged layer, inhomogeneous layer, film 2, composed of SiO, plus a-Si, on a c-Si surface. This model is in accord with all of our results and will therefore be used throughout this study. Fig. 1b also shows a typical fit of the data to the model with the parameters L_1 , L_2 , and volume fractions of constituents for film 2, and δ , the unbiased estimator which This model is considerably relates the quality of the fit. different from that found for the case of ion beam damage where film 2 was composed of c-Si, a-Si and voids. This suggests a different damage level and extent associated with ECR plasma processing. The BEMA fits also enable the extraction of SiO₂ film thicknesses which were independently checked by angle resolved xray photoelectron spectroscopy, from which the Si 2p spectra showed the presence of an SiO₂ film with a peak near 103.5 eV and the unoxidized Si peak near 99 eV. SiO₂ film thickness values obtained from the appearance of the Si substrate peak at various angles were compared with the SE BEMA value on the same sample. In one typical case XPS gave an average thickness of 6.7 \pm 0.5 nm and ellipsometry yielded a value of 7.2 nm.

Figure 2 shows the BEMA analyzed thickness values for film 1, the plasma oxide, and film 2 the interface damage layer as a function of oxidation time, for three substrate biases. We first focus on the longer oxidation times where a self limiting oxidation is seen without a sample bias. That the oxidation becomes self limiting implies that about a 3nm oxide provides a barrier to further oxidation which slows to produce less than 5 nm in two hours. With the addition of sample bias the situation is altered considerably. Specifically, the positive sample bias enhances the oxidation rate by five fold beyond a film thickness of 3 nm producing oxide at about 2.5nm/hr as compared to .5nm/hr for zero bias in the same thickness regime. Alternatively, the negative bias significantly reduces the rate, if not completely stops growth, in the same time interval. We therefore conclude that negative oxygen related plasma species are primarily responsible for the oxide growth in the transport limited regime beyond 3 nm, and this is in accord with previous marker studies of plasma

oxidation¹⁷.

In the very initial regime of growth below 3nm, the effect of bias is less clear. In Fig. 2 it is seen that in the initial regime all the applied sample bias conditions yield about the same oxidation rate. For an explanation consistent with the results, we first consider that the high density of electrons in the plasma promote electron attachment to O_2 via a favored interaction to produce a molecular ion, O_2^- , that is less stable than O_2 and more readily decomposes to atomic species¹⁸ according to the following:

$O_2 + e^- \rightarrow O_2^- \rightarrow O^- + O$

The O can readily migrate through the oxide with positive sample bias. For negative sample bias, however, the molecular ion O_2^+ predominates at the outer oxide surface, and this larger species (compared to O) is less likely to migrate rapidly through an oxide at low temperatures, or to decompose to atomic species. Prior to oxide barrier formation, when the oxide is too thin to present a diffusion barrier, the oxidant species react readily and similarly with the Si surface and bias presents only second order effects. In this case both bias polarities simply attract ionic species in addition to neutrals, thereby slightly increasing the oxidation rate over the unbiased case in the earliest oxidation regime.

As was mentioned above the damage layer observed as a result of ECR plasma oxidation shows no crystallographic damage in the Si surface, but rather an inhomogeneous oxide interlayer in between the c-Si substrate and stoichiometric SiO_2 . It is seen in Fig. 2 that for all bias conditions at least 3/4 of the damage layer forms

early (within seconds) in the oxidation process, and afterwards changes little with further oxidation. The fact that the damage layer reaches a steady state thickness is not easily rationalized. As the oxide film thickens, the Si surface should become further screened from exposure to damaging moieties from the plasma, and at the same time the damage at the Si surface is being consumed via the oxidation reaction. Thus, the consumption and screening of the Si surface suggests that a decrease in the damage layer is to be anticipated as oxidation proceeds.

The fact that a decrease in the damage layer is not observed during oxidation strongly suggests that the oxidation reaction itself, with the attendant large change in molar volume at the Si- SiO_2 interface during the conversion of Si to SiO_2^{19} can contribute to the damage layer in the form of a-Si, as is required by the BEMA in order to obtain the best fit. Considerable evidence exists (see for example the reviews refs 20 and 21 with references therein) which give evidence for a chemically and structurally disordered interfacial region as a result of oxidation alone. Furthermore, and more specifically, SE studies using BEMA analysis confirm that the Si-SiO₂ interface is best modeled using an interfacial layer that is composed of a volume fraction of a-Si²². This would be especially true for all temperatures below the Si crystallization temperature of about 500°C. It appears that oxidation significantly contributes to the damage layer when the ion or other damage mechanisms contribute little, namely when the total damage is small as with the ECR plasma.

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List of Figures

- Figure 1 (a) Typical spectroscopic ellipsometry pseudo-dielectric function spectra as a function of exposure time to the ECR Plasma. (b) Typical Bruggeman effective medium approximation, BEMA, fit of the data (open circles) to the BEMA for the model (solid line) using the optical model in the inset. The fit yields values for L_1 and L_2 and volume fractions of components and δ , the unbiased estimator, which measures the quality of the fit.
- Figure 2 ECR plasma oxidation results from the BEMA fits to the in-situ SE data yielding the oxide thickness (solid lines) and damage layer thickness (dashed lines) for various applied biases and at 0° incidence.







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