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### **APPLICATIONS OF SPECTROSCOPIC ELLIPSOMETRY TO MICROELECTRONICS**

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### ABSTRACT

Ellipsometry has been applied to problems in the microelectronics industry from the beginning in the 1960's. More recently spectroscopic ellipsometry has been introduced. In-situ during process ellipsometry offers great promise for monitoring and control of a wide variety of microelectronics processes. This review covers some applications in silicon technology such as oxidation, chemical vapor deposition, etching, interfaces, and new processing techniques such as plasma, ion beam and rapid thermal, in an effort to demonstrate the kinds of crucial microelectronics information and processes that modern ellipsometry can access. The conclusion is that single wavelength ellipsometry alone is not sufficient; spectroscopic ellipsometry is required to establish the optimum ellipsometry measurement conditions. The future of ellipsometry in microelectronics is assessed.

### INTRODUCTION

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There are many facets to modern microelectronics, but by far the largest is Si technology; this technology deals mainly with thin films and surfaces. Ellipsometry impacted this arena from the beginning in the 1960's as a film thickness measurement technique applied to dielectric films on Si, and mostly SiO, on Si<sup>1</sup>. This problem was broached at that time using single wavelength ellipsometry, SWE, with the good assumption for SiO<sub>2</sub> that k = 0 in the visible light range. Hence, the two measurables  $\Delta$  and  $\Psi$  at one wavelength,  $\lambda$ , and angle of incidence,  $\phi$ , are sufficient in principle to uniquely determine the film thickness, L, and refractive index, n. The rapidly advancing technology requiring thinner films, multiple film stacks, films with complex and variable stoichiometries, and better precision of L and n, led most of us to the conclusion that SWE alone is inadequate for many important applications. Furthermore, questions arose about the use of a discreet single film model to analyze the measurables<sup>2</sup>; there are physical issues such as interfaces between film and substrate that are not as sharp and flat as one might like and questions of stresses and stress gradients; there are chemical questions of stoichiometry and chemical gradients<sup>3</sup>. Each of these considerations added complexity to the ellipsometric measurement requiring more measurables than afforded by SWE. The solution to this dilemma in terms of ellipsometry is straightforward: use multiple  $\lambda$  and  $\phi$  which makes use of all the accessible variables in order to specify a system, hence spectroscopic ellipsometry, SE is required.

In this review applications of SE to Si based microelectronics process issues are emphasized, although most of the same issues and concomitant solutions exist within the other materials systems in microelectronics, viz. III-V and II-VI. The first issue addressed is the problem of the interface between film and substrate. What is new about the Si-SiO<sub>2</sub> interface and its measurement using SE, and how has ellipsometry and SE impacted this problem? The second issue is the use of novel process techniques such as plasmas, ion beams and rapid thermal systems. The measurement of temperature and surface damage are important and how has ellipsometry and SE helped to solve these problems? Finally, what is the role of ellipsometry in actual manufacturing processes? Ellipsometry has long been thought of as an esoteric specialists technique, but has it made an entry into the microelectronic manufacturing arena?

### MICROELECTRONICS PROCESSES

The major Si microelectronics process steps are shown in Table I. To date the film growth processes have received most of the attention from ellipsometry. Typically, film properties such as thickness and refractive index are measured ex-situ using routine automatic ellipsometers with significant component and  $\phi$  errors often greater than 0.1°. However, with the employment of thin films, the realization of the crucial nature of interfaces, and the need for process monitoring and control, is now clear to many of us that the era of "low end" ellipsometry use is over. What follows in this review is the discussion of several problems in microelectronics processing that have been impacted using ellipsometry. It is my thesis that SWE alone is no longer adequate, and SE is necessary. Nonetheless, a key idea that is developed in this review is that through the use of SE, SWE can often be rendered adequate for a specific measurement objective. This may be a major issue in the eventual use of ellipsometry in microelectronics manufacturing, since simplicity is necessary for the manufacturing environment.

Ellipsometry provides a non-destructive, non-invasive and accurate measurement of optical properties. In many important applications where an accurate optical model exists, SWE suffices, thus the measurement can be both simple to perform and readily interpreted. The relative nature of the ellipsometry measurement requires only weak light sources, hence the incident light usually does not alter the surface. Ellipsometry has been shown to operate in air, vacuum and liquids and the optical system can be positioned outside of a processing environment. Thus, it can be used to monitor processes under actual process conditions, hence it is non-invasive. The calculated results in Table II show that on a Si surface under the other conditions of the calculation,  $\Delta$  changes by about 0.3° per 0.1nm of overlayer film. Considering that a well aligned ellipsometer with high quality optics is capable of precision of about an order of magnitude better in  $\Delta$  and  $\Psi$  or 0.01-0.02°, sub monolayer sensitivity is achievable. To my knowledge, no other analytical technique has all of these advantages.

On the negative side, ellipsometry is a precision optical technique and therefore requires careful and expert alignment and calibration, in order to achieve the above optimum sensitivity. Most users do not know how to align and calibrate, and manufacturers have done little with hardware, software and education to overcome the difficulties. Hence many people only attain marginal results and simply don't believe the experts with their optimistic calculations.

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have the manufacturers from which they purchase an instrument achieve and teach them to achieve the literature SE spectrum of a freshly HF etched Si wafer. The well defined and sharp interband peaks with proper spectral positions, intensities and ratios are only obtained with a well aligned ellipsometer. For SWE the proper  $\Delta$ ,  $\Psi$  point for bare Si, thickness for a 10 nm SiO<sub>2</sub> film and index for a 100 nm SiO<sub>2</sub> film are also only achievable with a good instrument. Also, ellipsometry is not generally understood even by physicists. Thus, there is a reluctance about using ellipsometry that can be overcome with good software and powerful PC's with which a user can do a variety of calculations so as to obtain a substantive operational understanding of ellipsometry.

### FUNDAMENTAL RELATIONSHIPS

Ellipsometry measures the change in amplitude,  $\Psi$ , and phase,  $\Delta$ , between the p and s components of polarized light reflected from a surface. The measurables are cast as a complex reflection coefficient,  $\rho$ :

$$\varrho = \tan(\psi)\exp(i\Delta) = \rho(\phi,\lambda,N_{\mu}L_{\mu})$$
(1)

where N<sub>i</sub> and L<sub>i</sub> are the complex index and thickness of the i<sup>th</sup> component and with

$$\tan \psi = \frac{|r_p|}{|r_s|}, \ \Delta = \delta_p - \delta_s \tag{2}$$

with  $\delta$ 's as the phase angles and where

$$r_{p} = \frac{E_{rp}}{E_{ip}} = |r_{p}|\exp(i\delta_{p})$$

$$r_{s} = \frac{E_{rs}}{E_{is}} = |r_{s}|\exp(i\delta_{s})$$

The dielectric response function,  $\epsilon$ , or pseudodielectric function,  $\langle \epsilon \rangle$ , is then obtained directly from the measurement of  $\rho$ :

$$\epsilon \text{ or } <\epsilon > = \sin^2 \phi + \sin^2 \phi \tan^2 \phi \left[\frac{1-\rho}{1+\rho}\right]^2$$
 (4)

where

$$e = c_1 + i\epsilon_2 \tag{5}$$

and

$$e_1 = n^2 - k^2, \quad e_2 = 2nk \tag{6}$$

where n and k are the real and imaginary parts, respectively, of the complex index of refraction, N, given as:

$$N = n - ik \tag{7}$$

From a literature database for the known constituents of the film and substrate  $\rho_{cal}$  is calculated using the Bruggeman effective medium approximation discussed below, and compared with  $\rho_{exp}$  from equation (1) above and as a figure of merit for comparison, an unbiased estimator,  $\delta$ , is calculated from the relationship<sup>4</sup>:

$$\delta = \left[\frac{1}{N-P-1}\Sigma |\rho_{exp} - \rho_{cal}|^2\right]^{\frac{1}{2}}$$
(8)

where N here is the number of wavelengths sampled, and P the number of unknown parameters. A minimizing procedure gives the best fit parameters which are film thicknesses and percents for the constituents at 90 % confidence. It should be noted that the calculated  $\delta$  corresponds to a single wavelength measurement in spectroscopic ellipsometry since each  $\rho$  is at a wavelength. Thus, since one complete spectrum usually contains more than 50 wavelength points, the reported  $\delta$  is a simple average.

The Bruggeman effective medium approximation, BEMA, has been shown to be quite useful for calculating the dielectric response of mixed composition inhomogeneous films<sup>5</sup>. BEMA assumes mixtures on a scale smaller than the wavelength of light, but that each constituent retains its original dielectric response. One can imagine that this model might be appropriate for mixed phase films, large amounts of impurities in substrates and damage, and indeed these applications are extensively reported and some studies will be referred to herein. The generalized form for the BEMA is as follows:

$$\sum_{i} f_{i} \frac{\epsilon_{i} - \epsilon}{\epsilon_{i} + 2\epsilon} = 0$$
<sup>(9)</sup>

where  $\epsilon$  is the composite dielectric function, and  $\epsilon_i$  and  $f_i$  are respectively the dielectric function and volume fraction for the i<sup>th</sup> constituent. One useful recipe for the use of BEMA's is as follows:

1. Measure  $\Delta, \Psi$  and from equation (1) above obtain  $\rho$  and then from equation (4) determine  $\epsilon$ .

2. From other experiments, other information and/or good guesses, identify the constituents in the mixture.

3. Measure or find in the literature the 6's for the constituents.

4. From the general BEMA formula, fit the measured  $\epsilon$  with the available  $\epsilon_i$ 's. From this the f's are determined from the minimization.

Results using this algorithm will be shown below.

### SE VS SWE

The question of whether to use SE or SWE for a specific microelectronics problem is a valid one. SE will always yield more information, but the measurement is relatively time consuming and complicated, so the operational answer lies in equipment limitations principally speed and accuracy of the hardware, and most importantly a consideration of what is the desired result from the measurement. Speed is important when one desires to follow processes in-situ and during the processing. For example using a monochromator drive for SE in the visible range (200-800nm) could take 10 min or longer. However, with recent developments from Collins<sup>6</sup> laboratory using optical multichannel analyzers, OMA's, accurate SE scans can be made in the order of seconds, and if some precision can be sacrificed acquisition time of milliseconds is attainable. However, our experience to date is that once a particular process with the materials system is reasonably characterized. typically using SE and a variety of other in and ex situ techniques, SWE can be often employed to yield sufficient process monitoring information. This may not be the case with future more complex processes, but the examples to follow from our laboratory are of this type. Presently SE is a key technique in our laboratory used to characterize the system. and it is usually done in-situ and during process. SE is used to determine process variables, specifically the best optical models from which to interpret ellipsometric data. In the examples that follow we use SE and SWE in consort as the main techniques. However, a wide variety of surface analytical and microscopy techniques are required to establish appropriate optical models. It should be mentioned that the use of multiple angles of incidence also yields another method to enhance the acuracy of ellipsometry. However, this techniques has limited application for in-situ studies due to the fixed geometry restrictions of typical process chambers.

### **MICROELECTRONICS APPLICATIONS**

### Oxidation of Silicon, The Si-SiO<sub>2</sub> System

<u>Thermal Oxidation</u>. The thermal oxidation of Si provides a particularly appropriate example of the power of ellispometry in microelectronics. The traditional use of ellipsometry throughout the microelectronics industry was and still is to measure the resulting SiO<sub>2</sub> film thickness, L, and index of refraction, n. Since k = 0 is a good approximation for SiO<sub>2</sub> in the visible region (SiO<sub>2</sub> has a band gap of about 9 eV), an SWE measurement of  $\Delta$ ,  $\Psi$  enables the extraction of both desired parameters L and n. With a well aligned instrument and near half an ellipsometric period, n and L are obtained to an accuracy within a few percent. In the early 1970's two groups reported in-situ during oxidation SWE studies of the thermal oxidation of Si<sup>7.8</sup>. Figure 1a shows a sample of the data from our dry O<sub>2</sub> oxidation study from which the shape of the data was used to deduce and confirm oxidation models for the crucially important SiO<sub>2</sub> film growth process. Figure 1b from another in-situ during process SWE study<sup>9</sup> includes both dry and wet (H,O added)  $O_2$  oxidation of Si, and illustrates the great power of in-situ SWE for detailed and intricate studies of the oxidation reaction. The upper and lower solid lines show wet and dry results, respectively, as bounds. An initially dry  $O_2$  ambient is switched at some arbitrary time (100 min) to a mixture of  $O_2$  with  $H_2O$  (2000 ppm) whereupon the oxidation kinetics also abruptly changes to that for wet grown SiO<sub>2</sub>. The analysis of these SWE experiments using a single film or three phase model enabled a clearer understanding of the role of even trace amounts of  $H_2O$  on the SiO, film formation.

In the late 1970's several ellipsometric studies of the Si-SiO, interface<sup>10,11</sup> appeared that indicated that the system is not as simple as was first proposed. From a series of SWE measurements it was deduced<sup>10</sup> that n for SiO<sub>2</sub> was in fact different for different SiO<sub>2</sub> film thicknesses. Specifically, the index rises as the film is thinned. A model including a transition layer was proposed. The emergence of SE provided an important confirmation of this result<sup>11</sup> and enabled a more detailed model of the interface afforded by the prodigious spectral data from SE as compared to SWE. In order to illustrate this important finding, we show in Figure 2a our data for a 3 nm oxide film which demonstrates the essence of the idea. We analyze the same SE data set using three different optical models. It is seen that the simple homogenous SiO, film model yields the worst fit, and the debate continues to this day as to which of the interface models is best, but there is no doubt that an interface region with different optical properties is identified. The effect of neglecting this interface layer can be evaluated by examining different thicknesses. Figure 2b is SE data analyzed using a single homogenous film model and shows that for films greater than 5 nm the effect of neglecting the presence of the interfacial region in minimal. This fact results from the progressive insensitivity of ellipsometry to the film covered interface as half period is approached.

In order to circumvent this sensitivity problem and be able to investigate the interface under a wide variety of conditions, we need to somehow remove the optical response of the top (ambient-SiO<sub>2</sub>) interface. To this end, we have developed an immersion ellispometry technique<sup>12,13,14</sup> in which the film covered substrate is immersed in a liquid that refractive index matches to the overlayer. It is important that the immersion liquid also has a spectral window in which to do SE. Assuming that the interface region is optically distinct from the bulk film, an assumption borne out in numerous experiments<sup>10,11,15</sup>, then there will be enhanced sensitivity to the interface region. Calculations shown in Figure 3a of the change in  $\Delta$  as  $\delta \Delta$  (and  $\delta \Psi$ ) with and without an assumed interface indicate about an order of magnitude enhancement in the sensitivity of the interface region using CCl, rather than air as the immersion medium. Figure 3b shows unmodeled results of the significant changes that take place in the interface region from post oxidation annealing. This data was modeled using an inhomogeneous interface layer in between the Si substrate and SiO<sub>2</sub> film overlayer and containing suboxide and Si surface protrusions (Si roughness). From this model relevant interface parameters are extracted<sup>12,13,14</sup> and comparisons can be made with other measurements for example AFM measurements of roughness. Also indicated on this Figure are the physical processes that we believe are operative in the different temperature regimes for the post film growth annealing. This work continues in our laboratory with the objective to refine the interface layer model.

The relevance of the above studies for the present review is that to actually follow the progress of microelectronics processes, it is not always necessary nor even desirable to perform SE in real time. However, SE is used to establish the best optical model that can then be used at an opportune  $\lambda$  to then follow a process using SWE. This methodology pervades all our SE and SWE studies and will be illustrated further below.

<u>Plasma Oxidation</u>. In the past several years we have constructed ellipsometric hardware to follow electron cyclotron resonance, ECR, plasma oxidation and chemical vapor deposition of a variety of films (oxides, nitrides and Si) on a variety of semiconductor substrates, viz. Si, Ge, and InP using SE and SWE. The ECR process is important, because it enables the preparation of desired thin film materials at low process temperatures to limit solid state diffusion, and with low ion energies to minimize damage to the semiconductor. Below, we specifically address the issue of ion damage, but suffice for now that much of the damage resulting from ion and plasma exposure during semiconductor processing (cleaning, film growth and etching) can be modelled using an inhomogeneous interface layer using the BEMA, as was done above for Si thermal oxidation. We restrict the present discussion to the Si situation where the interface layer typically contains a-Si, c-Si, SiO<sub>2</sub> and voids. Analogous situations obtain for the other semiconductor systems.

Before the ECR plasma oxidation mechanism can be explored using in-situ during process ellipsometry, the appropriate optical model is required. Figure 4a shows typical SE oxidation data<sup>16,17,18</sup> in terms of the dielectric function from which the time evolution of the process is observed. Figure 4b shows the four models considered for analysis of the data. Underneath each model is the value for the unbiased estimator,  $\delta$ . In all cases studied the unbiased estimator for model 4 was about 1/2 of the smallest value for the other sensible models. None of the fitting improved with the addition of voids and for model 4 about 50% a-Si and 50 % SiO<sub>2</sub> was obtained for the volume fractions of constituents. Figure 4c shows the results calculated from model 4 for several D.C. substrate biases in terms of the thicknesses for the oxide and interface layers. The instantaneous formation and thereafter small change in the interface layer as well as the bias effects on the oxide layer enable elucidation of the oxidation mechanism.

Figure 5 is a set of our SE spectra for Si, Ge, InP and InSb taken in-situ at temperatures up to 300°C. While it is anticipated that the dielectric spectra would be a function of temperature<sup>19,20,21</sup>, one readily notices that there is a narrow region of the spectrum for all these semiconductors and near 3.65 eV for Si which is relatively temperature insensitive. Additionally, one can see that at other spectral regions, near 3 eV for Si, there is greater temperature sensitivity. We return to this latter point below, but it is instructive to point out that the great power of SE is to explore the spectra for further information about the system under study and then to design simple hardware for a particular  $\lambda$  for a specific application. We have loosely called these specific wavelengths that optimize a particular SWE measurement for a given material, "magic wavelengths". For example for Si the temperature insensitive 3.65 eV energy is particularly appropriate for ECR plasma studies, because with the substrate exposed to the plasma during processing, the substrate temperature rises by less than 100°C, but the specific amount

depends on time and process. However, with the use of the 3.65 eV light this small change can be ignored. Figure 6 shows the SWE results at 3.65 eV in terms of the total film thickness (oxide and interface layer) versus oxidation time at several substrate biases. From this data and the SE results above, we were able to model the results based on the Cabrera Mott theory and we found the interface or damage layer was about the same as for thermal oxidation. In fact for the ECR plasma oxidation of Si, Ge and InP the results are quite similar to thermal oxidation results. To us this conclusion is contrary to intuition, because of the apparent lack of correspondence of the ECR and thermal environments.

### **RAPID THERMAL PROCESSES**

Rapid thermal processing, RTP, enables thermally activated processes to occur such as oxidation, RTO, and CVD, RTCVD, without excessive time at temperature. For modern devices with features smaller than 200nm the time at temperature is crucial, since solid state diffusion of dopants will alter if not destroy device action. One problem with RTP is the lack of a satisfactory method for temperature measurement. Optical pyrometry is commonly used, but its accuracy depends on a knowledge of surface emissivity which changes due to both temperature, T, and processing. However, from our earliest SWE experiments<sup>8</sup> of the in-situ during process oxidation of c-Si, we used the measured temperature dependence<sup>19</sup> of n and k, in order to reduce the data that was obtained at process temperatures of 800°C and above. Thus, it appeared possible to use this temperature dependence to extract T from the measurement of  $\epsilon$  or n and k. For this purpose, we constructed the rapid thermal system shown in Figure 7. Heating is accomplished using banks of quartz iodine lamps with the light falling on the backside of the Si wafer. Ellipsometry is done on the wafer front side and the wafer isolates the lamp light from the ellipsometric measurement.

Figure 8 displays the  $\Delta$ ,  $\Psi$  mapping of SiO<sub>2</sub> film thicknesses on Si at near room temperature (labelled as 0) and 1100°C<sup>22</sup>. From this it is recognized that both thickness and temperature could be obtained from the unique mapping. Thus, we believed that we could measure both T and L from a single SWE measurement. From polynomial fits to the calculated trajectories, the desired T and L parameters could be rapidly obtained with a PC. The system was automated and SWE measurements using a HeNe laser at 632.8 nm (1.96 eV) provided real time control of the process with feedback to recognize the desired process set points<sup>23</sup>. Figure 9a shows the result of SWE measurements of T where the set point is 950°C and 9b with the thickness set point of 10nm. Using 632.8 nm light T precision against a thermocouple was within 18°C rms, and thickness within a few tenths of a nm or 3%. It is interesting to notice from Figure 5 above that below 2.5 eV (near 2 eV for 632.8nm) is not ideal for T sensitivity, although convenient in terms of an available and stable light source. Indeed, as was mentioned above 3 eV should significantly improve the precision. We calculate about a fourfold improvement in T sensitivity for 3 eV, and experiments are now underway.

In this application SWE was used for the real time measurement, but once again SE provided the information needed to understand the process and then to design for optimum measurements.

### ION BEAM DAMAGE AND ETCHING

The many repetitive film deposition and removal process steps require monitoring of ~uality and end points. To these ends, we show examples of in-situ during process applications of ellipsometry for both dry ion beam processing and wet chemical etching.

The dry processes involve the interaction of directed ion and neutral reactive fluxes obtained from ion beam sources and plasmas. Oftentimes, the surface processed using energetic techniques is degraded. It would be useful to have a quick in-situ during process measurement of the damage, because the usual analytical techniques that access surface damage are destructive (RBS channeling, TEM) or cannot operate during processing (XPS, LEED) or both, and usually time consuming as well. As mentioned above ellipsometry overcomes all of these difficulties. The issue is whether useful optical models can be obtained that yield damage parameters and then used for in-situ during process We do not repeat here the pioneering studies<sup>24,25,26,27,28,29</sup> which measurements. establish the use of ellipsometry, and the BEMA to study surface damage. The essential point is that damage can be measured with a damaged layer model that assumes that an inhomogeneous, but discrete damage layer exists on the substrate surface which may be covered by an overlayer. For bare Si surfaces this damage layer includes a-Si, c-Si and voids. When oxygen is present, typically as an SiO, layer either native, adventitious or intentional, the model is extended to two layers where the top one is damaged oxide modeled as a mixture of SiO<sub>2</sub>, a-Si and sometimes voids. Different experimental circumstances determine the specific applicable model, and typically many likely permutations are tried along with the use of results from other measurements when a particular process is studied. In this way a particularly well suited model is obtained.

Figure 10a shows the changes in the in-situ during process SE obtained dielectric spectra for a Si surface bombarded with 1200 eV Ar ions for various ion doses which translate to process times. A shutter placed between sample and ion flux was used to interrupt the bombardment and collect a SE spectra. This is a limitation of our apparatus with a scanning monochrumator and PMT, but not to more advanced systems<sup>6</sup>. Saturation is seen for all energies. Figure 10b shows saturation spectra for different energies. Figure 10c shows the typical high quality fit of the spectrum for a native oxide covered Si surface exposed to Ar ion bombardment. In the two layer model, L<sub>2</sub> represents the extent of the damage layer adjacent to the c-Si substrate and  $L_1$  represents the damaged oxide overlayer. Figure 11 shows the analysis of the data in Figure 11a in terms of  $L_1$  and  $L_2$ .  $L_1$  is nearly constant at 2 nm while the damage layer L<sub>2</sub>, the amorphized layer, grows with higher energies otherwise the nature of the damage is remarkably constant. This level and extent of damage has been studied by TEM with considerable agreement both on the nature and the extent of the damage<sup>24,26,29</sup>. Of particular interest is the analyzed data for an Ar ion bombarded SiO, covered Si surface with about 17 nm SiO. in Figure 12. It is worthwhile to observe that the damage layer, L<sub>2</sub>, grows slowly with time (dose) compared with the nearly bare Si surface above, and there is a decreasing oxide overlayer thickness, L<sub>1</sub>. The reason for this is because the amorphizing ion dose must reach the Si to cause damage, i.e. the ions must first penetrate the oxide. Initially, the unthinned oxide effectively blocks the ions and prevents damage. However, as the oxide thins, ions eventually reach the Si

surface. Hence, there is an ion energy dependent lag between the etching and the growth of the damage. It is impressive that these events can be followed with considerable precision with in-situ during process SE.

For H ions the situation is more complicated and studied in some detail<sup>26,31,32,33</sup>. We show in Figure 13 a very interesting study that led us to an improved recipe for H surface cleaning with minimum damage. Figure 13a shows the saturation SE spectra for the 13.3 nm SiO<sub>2</sub> covered Si surface upon H ion bombardment, while Figure 13b shows the analyzed spectra using a bar like representation for the layers present. The comparison of several H treatments of the oxide covered Si surface shows that the lower energy, 300 eV, treatment with heating during bombardment, 450°C, process e, yields reasonable oxide removal rates with minimum damage in the Si. Prior to our SE study the best recipe for oxide removal via H ions<sup>34</sup> was using higher energy H ions, treatment d, but this study did not measure surface damage, and resulted in a larger damage layer. SE studies also revealed that it was far more efficient to anneal damage during ion bombardment than afterwards.

The above studies of Ar and H ion beam treatments are with the use of low energy ions of about 1 keV and below. There are numerous studies of higher energy ion implantation and damage studies where SWE and SE were used to measure damage.

The Ar and H ion beam treatments were attempts to develop Si surface cleaning processes in the dry media compatible with vacuum processes. While this application is an important one for advanced microelectronics processing, most semiconductor surface preparation and cleaning is performed in liquid media. Ellipsometry can readily make accurate measurements in liquids, if care is taken about the fact that the incident light path will be altered upon entry of a medium of different refractive index.

Figure 14a shows our results<sup>35</sup> for the etching of SiO<sub>2</sub> in terms of SiO<sub>2</sub> thickness versus time in dilute HF as was followed by real time SWE. It is seen that the etching can be followed and that the SiO<sub>2</sub> film thickness does not decrease to zero. Figure 15b shows the  $\Delta, \Psi$  data. From this unmodeled data we can see that initially the  $\Delta, \Psi$  values approach those for bare Si, but then as exposure to the solution continues the data moves in a parallel  $\Delta, \Psi$  trajectory indicative of a different film forming. Other measurements<sup>36</sup> indicated that the hydrophobic surface that formed is likely an H terminated surface.

### THE FUTURE FOR ELLIPSOMETRY IN MICROELECTRONICS

The above cited microelectronics examples of the applications of in-situ during process SE and SWE comprise a sampling of our research groups attempts to use ellipsometry for microelectronics applications. It is clear from this small set of studies that ellipsometry, both SE and SWE, has a major role.

Recently, the concept of "single wafer processing" has been proposed for microelectronics manufacturing. I believe that this concept will prompt a renaissance for ellipsometry in microelectronics. The "single wafer processing" concept is the use of vacuum processes in sequence. Many of the vacuum processes, such as the plasma and ion beam processes of deposition, etching and cleaning, among many others were developed in basic research laboratories where careful and skilled experimentation, and not manufacturing takes place. However, with the availability of large diameter virtually perfect single crystal Si wafers (larger than 150mm), the projected decrease in device feature size below 160 nm, and the rapid rise in the expense of clean room process facilities, batch processing no longer represents the best engineering. A modern single wafer process is projected to out produce present batch processing.

In order to effectively utilize single wafer processing, competent process monitoring and control must exist. One cannot wait until a process step ends to perform diagnostics and make process improvements. These requirements translate into real time measurements with sensitivity and accuracy. Ellipsometry has been shown to have the competence. The goal of my presentation was to indicate this competence.

The hardware for "single wafer processing" is vacuum process chambers connected together with wafer transfer capability and equipped with in-situ process monitors. Ellipsometry under computer control has been shown to be compatible with all the required processes, viz. it is a universal technique particularly well suited to microelectronics where thin films on nearly perfect surfaces are common.

What is needed and what is the future for SE in microelectronics? First, more applications of real time control need to be demonstrated, but I am certain that this will be forthcoming. The science and scientists are presently sufficient yet better and more science is also emerging (a particularly good example is the Collins paper). Next. ellipsometry hardware needs to be truly compatible with process chambers. Despite improvements with in-situ systems there is much to be done before the sensitivity and accuracy inherent with ellipsometry is realized with commercial in-situ systems and certainly before a hard nosed process angineer will use ellipsometry to control his process. Calibration and alignment procedures have not been significantly improved in twenty years. I think that the development of specific ellipsometers for specific microelectronics measurement tasks with customized software is important. The use of "magic wavelengths" is one approach to this notion, since a simpler and more robust machine can be designed. The role of SE might then be to aid the development of specific machines. This kind of ellipsometer development will require ellipsometry people to understand microelectronics needs.

The good news is that the field of "single wafer processing" is ripe for ellipsometry. Indeed, ellipsometry, at least SWE, is being widely used for in-situ applications in development laboratories but not yet in manufacturing. SE is far less used. The less than good news is that progress with hardware must be swift to take advantage of the present opportunity, but little progress is in evidence.

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### List of Figures

Figure 1. Results from in-situ SWE employed during the Si oxidation process: (a) dry  $O_2$  results; (b) dry and wet  $O_2$  results.

Figure 2. SE data and models for the Si-SiO<sub>2</sub> interface: (a) thin film data analyzed with three models; (b) thicker film data analyzed with a single homogenous film model.

Figure 3. Immersion ellipsometry studies of the Si-SiO<sub>2</sub> interface: (a) estimation of sensitivity in terms of the change in parameters,  $\delta\Delta$  and  $\delta\Psi$ , with and without an assumed interface layer in air and CCl<sub>4</sub>; (b) post oxidation annealing results representated in terms of the change of  $\Delta$  before and after annealing, the effective interface parameter.

Figure 4. Electron cyclotron resonance plasma oxidation results: (a) SE data in terms of  $\epsilon$  at floating substrate temperature; (b) models with best fit unbiased estimator,  $\delta$ ; SE oxidation results at several substrate biases analyzed according to Model 4.

Figure 5. SE spectrum of Si, Ge, InP and InSb up to 300°C.

Figure 6. SWE ECR plasma oxidation of Si results with (a) D.C. substrate biases and (b) temperatures. Total film thickness is reported.

Figure 7. Rapid thermal process, RTP, system with SE.

Figure 8.  $\Delta, \Psi$  map for SiO<sub>2</sub> films on Si at two temperatures.

Figure 9. Rapid thermal oxidation, RTO, process under ellipsometric control: (a) process temperature versus time; (b)  $SiO_2$  film thickness cata versus time.

Figure 10. Results from  $Ar^+$  bombardment of Si and SiO<sub>2</sub>: (a) SE spectra of 1200 eV and at various doses (times); (b) saturation spectra at various ion energies; (c) best fit model.

Figure 11. Analyzed results of Figure 10 in terms of the damage layer,  $L_2$  and native oxide damaged overlayer,  $L_1$ .

Figure 12. Analyzed results of Ar ion etching of a SiO<sub>2</sub> film of thickness  $L_1$  and evolution of the damage layer,  $L_2$  for two ion energies.

Figure 13. H ion etching of SiO<sub>2</sub> on Si: (a) SE data for five different processes when spectra no longer change (at saturation); (b) analyzed SE data from (a) in terms of a two layer model.

Figure 14. In-situ SWE etching results of SiO<sub>2</sub> film on Si in HF solution: (a) SiO<sub>2</sub> thickness changes; (b)  $\Delta$ ,  $\Psi$  data for the etching results.

SILICON PROCESS STEP	PROPERTY BY ELLIPSOMETRY
Crystal Growth	Solidification
Wafering	Surface Quality
Oxidation	Film Thickness & Index
Chemical Vapor Deposition	Film Thickness & Index
Cleaning	Surface Quality
Etching	Film Thickness & Damage
Metallization	Morphology
Lithography	Resist Thickness

Δ	¥	Thickness (nm)
179.257	10.448	0.0
178.957	10.448	0.1
178.657	10.449	0.2
178.356	10.450	0.3
178.056	10.451	0.4
177.756	10.453	0.5
176.257	10.462	1.0

Conditions: Film with index = 1.5 on Si,  $\lambda = 632.8$  nm,  $\phi = 70^{\circ}$ 

Sensitivity: about  $0.3^{\circ} \Delta$  Per 0.1nm film thickness.

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# **TEMPERATURE EFFECTS**





Fig 16



Thermal SiO<sub>2</sub> on Si



# Thermal SiO<sub>2</sub> on Si







4a

# OPTICAL MODELS FOR ECR PLASMA OXIDATION





## DIELECTRIC FUNCTIONS WITH TEMPERATURE



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# Si Damage With Dose





Si Damage With Energy



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# Bruggeman EMA Fit

600 eV, 5 x 10  $^{15}$  cm $^{-2}$  Ar $^+$ 





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# **Bruggeman EMA Results**

Etching SiO<sub>2</sub> on Si With  $\Lambda r^+$ 



H<sub>2</sub><sup>+</sup> ETCHING OF SiO<sub>2</sub> ON Si



H<sub>2</sub><sup>+</sup> ETCHING OF SiO<sub>2</sub> ON Si

CONDITIONS	0	a	ď	C	d	e
TOP LAYER	SiO <sub>2</sub> 100%	SiO <sub>2</sub> 91% a-Si 9%	SiO <sub>2</sub> 94% a-Si 6%	SiO <sub>2</sub> 100≹	a-Si 100%	a-Si 100%
OVERLAYER	a-Si 100%	Void 20% a-Si 71% c-Si 9%	Void 43% a-Si 52% c-Si 5%	Void 25% a-Si 41% c-Si 34%	Void 11% a-Si 22% c-Si 67%	Void 62% a-Si 6% c-Si
THICKNESS (Å)	6	390	67 63	33 149	11 95	12 4
UNBIASED ESTIMATOR	<b>0.010</b>	0.011	0.012	0.020	0.015	0.018

- o before bombardment, 13.3 nm SiO<sub>2</sub> on Si
- a 1000 eV  $H_2$  ion, 25°C, normal
- b 1000 eV  $H_2$  ion, 450°C, normal
- c 300 eV H<sub>2</sub> ion, 25°C, 60°
- d 1000 eV  $H_2$  ion, 500°C, 60°
- e 300 eV H<sub>2</sub> ion, 500°C, 60°

# Oxide Thickness vs. Etch Time



PSI vs. Delta for HF Etch Experiments



Gould and Irene, J. Electrochem. Soc. ,135, 1535(1988)

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