ELLIPSOMETRY STUDIES OF SEMICONDUCTORS SURFACE CLEANING

E.A. Irene & Y.Z. Hu
Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290

Submitted to:
Proceedings of MRS Symposium on Cleaning

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.
Ellipsometry Studies of Semiconductors Surface Cleaning

E.A. Irene & Y.Z. Hu

The University of North Carolina
Chemistry Department
CB #3290 Venable Hall
Chapel Hill, NC 27599-3290

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

None

This document has been approved for public release and sale, distribution of this document is unlimited.

Ellipsometry is shown to provide a sensitive evaluation of the surface cleaning process based on in-situ and ex-situ studies of the cleaning of Si, Ge, and InP surfaces. Both single wavelengths and spectroscopic ellipsometry are shown to be applicable. The essentials of the measurement and sample results are discussed.

Ellipsometry, surface cleaning

Unclassified

Unclassified

Unclassified
ABSTRACT

Ellipsometry is shown to provide a sensitive evaluation of the surface cleaning process based on in-situ and ex-situ studies of the cleaning of Si, Ge, and InP surfaces. Both single wavelength and spectroscopic ellipsometry are shown to be applicable. The essentials of the measurement and sample results are discussed.

INTRODUCTION

During the early years of Si technology, cleaning and initial Si preparation consisted of wafer degreasing, acid baths and clean water rinsing. The use of HF dipping came into the processing early as it was recognized that HF could remove an oxide and not readily attack the highly polished Si surface. The production of a hydrophobic Si surface after HF etching was thought by some to be clear evidence for the production of a clean bare Si surface. Now we all realize that HF does not leave a bare Si surface but rather an H terminated Si surface. Additionally, and most importantly when this hydrophobic Si surface is oxidized, an electronically excellent Si-SiO\textsubscript{2} interface is produced.

Owing to both the simplicity and effectiveness, wet cleaning of Si is the most commonly practiced method for microelectronics processes. Usually some form of RCA cleaning is used followed by an HF or buffered HF dip with déionized, DI, water, rinsing after each step. While many variations of this simple procedure exist, this basic procedure is routine in Si microelectronics and similar processes are used for other semiconductors. In addition for single wafer processes, where vacuum chambers are used for the processing and for epitaxial film preparations it is useful to develop all dry processes that can be performed in the processing chambers. To these ends, ion beams and plasmas, often with H, are used to remove surface layers. With the use of energetic processes, damage to the surface can occur, and this could obfuscate the otherwise good effects of cleaning. Also, it is desirable to be able to monitor the cleaned semiconductor substrate and the cleaning process non-destructively and non-invasively in both wet and dry environments. This is a complex task, yet ellipsometry has already been shown to be competent.

In this paper the use of ellipsometry, both spectroscopic ellipsometry, SE, and single wavelength ellipsometry, SWE, is demonstrated to monitor the semiconductor surface cleaning process. The basic principles are presented first and several examples taken from our recent work are presented to illustrate the kinds of results obtainable.

THE ELLIPSOMETRY MEASUREMENT

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, \( \rho \):
\[\rho = \tan(\psi) \exp(i\Delta) = \rho(\phi, \lambda, N_i, L_i)\]  \quad (1)

where \(N_i\) and \(L_i\) are the complex index and thickness of the \(i^{th}\) component and with

\[\tan \psi = \frac{|r_p|}{|r_s|}, \quad \Delta = \delta_p - \delta_s\]  \quad (2)

with \(\delta's\) as the phase angles and the \(r's\) are the complex Fresnel coefficients. The dielectric response function, \(\epsilon\), or pseudodielectric function, \(<\epsilon>\), is then obtained directly from the measurement of \(\rho\):

\[\epsilon \text{ or } <\epsilon> = \sin^2 \phi + \sin^2 \phi \tan^2 \phi \left[ \frac{1 - \rho}{1 + \rho} \right]^2\]  \quad (3)

where

\[\epsilon = \epsilon_1 + i\epsilon_2\]

\[\epsilon_1 = n^2 - k^2, \quad \epsilon_2 = 2nk \quad \text{and} \quad N = n - ik\]  \quad (4)

where \(n\) and \(k\) are the real and imaginary parts, respectively, of the complex index of refraction, \(N\).

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

The Bruggeman effective medium approximation, BEMA, has been shown to be quite useful for calculating the dielectric response of mixed composition inhomogeneous films\(^5\). 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.

Ellipsometry as a relative measurement (see eqn (2)) does not require intense light sources and thus provides a non-destructive measurement; and because the required optics can be placed outside the process chambers it is also non-invasive. In many important applications where an accurate optical model exists and the system has been well characterized, SWE suffices, thus the measurement can be both simple to perform and readily interpreted. Ellipsometry has been shown to operate in air, vacuum and liquids and thus applicable to many microelectronics processing environments under actual process conditions\(^6\).

A calculation shows that on a Si surface \(\Delta\) changes by about 0.3° per 0.1nm of overlayer film with \(n = 1.5\) at \(\lambda = 632.8\) and \(\phi = 70°\). Considering that a well aligned ellipsometer with high quality optics is capable of precision in \(\Delta\) and \(\Psi\) of about 0.01-0.02°, sub monolayer sensitivity is readily achievable.

In addition to the use of ellipsometry with an optical model from which optical properties can be obtained, the measured dielectric functions can provide a sensitive and model independent assessment of surface condition. Aspnes has shown\(^7\) that for a three phase system (ambient, film, substrate) where the dielectric function of the substrate, \(\epsilon_s\), is much larger than that for the film, \(\epsilon_f\), which is in turn greater than that for the ambient, \(\epsilon_a\) (for air \(\epsilon_a = 1\)) the pseudodielectric function is given as:

...
Figure 2a shows calculated $\epsilon$ spectra in the visible range for different SiO$_2$ thicknesses on Si. It is seen that the spectra, both $\epsilon_1$ and $\epsilon_2$, change by an amount proportional to thickness of the SiO$_2$ overlayer. The direction of the change from the bare Si is different in different spectral regions, as is the magnitude. Equation (5) teaches that the use of the most surface sensitive spectral region would maximize the change, and the direction of the change for a transparent overlayer is predicted to be towards lower values of $\epsilon_2$. This condition is met near the $E_2$ peak for Si (4.4 eV) which is the maximum optical absorption region, and hence yields the greatest surface sensitivity for $\epsilon_2$. This is confirmed in Figure 2a which displays the largest negative change at the $E_2$ peak (about 4.4 eV) as the overlayer grows. The same situation would prevail for all overlayers that meet the conditions of equation (5) which would likely include oxides, nitrides, fluorides and organics, viz. the kinds of overlayers expected for the cleaning of semiconductor surfaces. A calculation was performed using the Bruggeman effective medium approximation, BEMA, to simulate a rough Si surface where the roughness is considered to be a film of mixed composition (50% a-Si plus 50% voids) with a thickness on the Si substrate. The resulting SE spectra are qualitatively indistinguishable from film growth. Figure 2b shows experimental ex-situ SE results for cleaning of Si. As the surface is cleaned the $E_2$ peak rises. After the usual RCA clean, HF dip and DI water rinse it is clear that an overlayer exists on Si.

![Figure 2a](image1)

**Figure 2.** (a) Shows calculated SE spectra for different thickness ($L_{ox}$) SiO$_2$ films on Si and (b) show experimental results with and without cleaning with a reference spectrum.

Figure 3a shows the SE ex-situ results for the cleaning of Ge. The chemical cleaning procedure consisted solvent degreasing and HF dip followed by DI water rinsing. It was found that if a thermal preoxidation and another HF dip was done the dielectric function was that for bare Ge. This Figure also shows the excellent fitting of the data to a three phase model: air ambient, inhomogenous native oxide film composed of GeO$_2$ and a-Ge, Ge single crystal substrate. This is the same model used for Si cleaning and was established using both SE and XPS measurements.

Figure 3b shows the SE ex-situ results for the wet cleaning of InP. Samples X
and Y were from different vendors. We found that the cleaned X samples gave the most consistent spectra and closest to the data base for bare InP. It is seen that degreasing alone (degreasing: 5 min dip in each of trichloroethylene, methanol, and flowing deionized water) yielded an overlayer on the surface. The etching step was necessary (etching: dip for 20 s in HF(48%):MeOH = 1:40 followed by a MeOH rinse for 2 min).

![Graphs showing various cleaning procedures for Ge and InP surfaces.](image)

**Figure 3.** Various wet cleaning procedures applied to a) Ge and b) InP surfaces with reference spectra.

**DRY CLEANING OF Si**

Figure 4a shows in-situ SE $\varepsilon_2$ spectra for the $\text{H}_2^+$ ion cleaning of SiO$_2$ covered Si surfaces using five different cleaning procedures labelled a-e$^8$. It is seen that process e yields a spectrum very close to that for bare Si (see Fig 3), and thus is the desired cleaning process. The others all have some measure of ion damage which has the effect of lowering and broadening the peaks in $\varepsilon_2$. It is interesting that process d was reported$^{16}$ to be a good procedure for Si dry cleaning as was determined using in-situ Auger spectroscopy. Figure 4b shows some of our newest Ar ECR plasma experiments where we removed SiO$_2$ from Si using a - substrate bias. No etching was observed for 0 or + biases indicating that Ar$^+$ is the etching species.

**CONCLUSIONS**

It was illustrated with examples from recent Si, Ge and InP studies that both SE and SWE can be used to sensitively monitor cleaning of a surface in-situ and ex-situ. Depending on the existing knowledge about the system, model dependent parameters or model independent measurables are used. SWE provides simple, fast measurements to monitor a cleaning process in-situ in virtually any process environment while SE provides model information about the process.
Notice that the measured dielectric function for the overlayer and substrate is a function of thickness and the dielectric function for the substrate, \( \epsilon_s \), but not for the film, \( \epsilon_f \). The presence of the overlayer is to modify the dielectric function of the substrate, \( \epsilon_s \). Experimentally this condition can be achieved at the maximum in \( \epsilon_s \) for the substrate and for a transparent film. The use of this technique will also be illustrated.

WET CLEANING OF Si, Ge AND InP

Figure 1 shows in-situ (in liquid) SWE results of HF treatment of SiO₂ covered Si. In Figure 1a the unmodeled \( \Delta, \Psi \) trajectory shows that etching of the SiO₂ proceeds as expected with the removal of oxide (increase in \( \Delta \) and decrease in \( \Psi \)) until the Si surface is neared. Then the trajectory proceeds back towards decreasing \( \Delta \) and increasing \( \Psi \) but not on the original SiO₂ trajectory. This is indicative of the formation of a different overlayer with a different \( N \). The identity of this thin overlayer cannot be determined using ellipsometry alone except to notice that \( N \) for this new overlayer is greater than that for SiO₂. Other studies reveal that this film could be H terminated Si and/or organic impurities adsorbed onto the Si surface. Figure 1b shows the same data in 1a, but modeled in terms of a three phase model: ambient, SiO₂ film, Si substrate. From the modeled result it appears that the etching ceases near 2 nm which is different from the above interpretation of Figure 1a. This situation points to the dangers of using a model that is incorrect whereupon the model constrains the obtainable parameters. From these results the recommended ellipsometry procedure is to use the measured data, \( \Delta, \Psi \) for SWE as shown above or \( \epsilon \) for SE.

\[
\langle \epsilon \rangle = \epsilon_s + \frac{4\pi id}{\lambda} \epsilon_s^{\frac{3}{2}}
\]

(a) (b)

Figure 1. Dilute HF etching of SiO₂ followed by in-situ SWE: a) shows unmodeled data and b) shows the same data modeled using a one film model.
ACKNOWLEDGEMENT

This research was supported in part by the Office of Naval Research, ONR, and the National Science Foundation, NSF.

![Graph](image)

Figure 4. a) shows various H⁺ ion beam cleaning procedures applied to SiO₂ on Si: o. before etching: a. 1000 eV, 90°, 25°C; b. 1000 eV, 90°, 450°C; c. 300 eV, 60°, 25°C; d. 1000 eV, 60°, 500°C; e. 300 eV, 60°C, 500°C. b) shows Ar ECR plasma etching of SiO₂ at -80V substrate bias and two different angles.

REFERENCES