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In situ characterization of SiO₂ etching with second harmonic generation and ellipsometry

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Abstract

The etching process of SiO₂ films on Si(111) was studied by in situ second harmonic generation (SHG), linear reflectivity and ellipsometry. All measurements are very well described with one simple model, with only the etching speed as adjustable parameter. In contrast to the linear optical measurements SHG shows high interface sensitivity when the silicon is etched clean.

Keywords: Crystalline–amorphous interfaces; Ellipsometry; Etching; Second harmonic generation; Silicon oxides

1. Introduction

Si–SiO₂ is probably one of the most intensively studied, yet still poorly understood, interfaces of the past decades. The trend to even further reduce the gate oxide thickness in IC technology, calls for a still better understanding and control of the electronic properties of very thin silicon oxide layers. Over the past decade second harmonic generation (SHG) has been developed into a versatile and sensitive surface and interface probe [1–3]. SHG has recently been used to study a number of properties of the Si–SiO₂ interface, including steps and kinks [4,5], strain [6,7], preparation and roughness [8] and electric fields [9]. Recently we have shown that the strong thickness dependence of the s-polarized SHG from thick thermal oxides on Si(111) is completely explained by linear optics, due to multiple reflections in the oxide layer [10,11]. The model combined the calculation of the Fresnel coefficients for the three-layer system (air–oxide–silicon) [12], with the well-known phenomenological model for SHG [13–16]. It was also shown that the amplitude of the SHG signal from thin (~ 2 nm) oxides depends on the thermal history of the oxide [10]. In this paper we report on simultaneous in situ SHG and linear reflectivity measurements during the etching of high quality SiO₂ films on Si(111). For the same process parameters also in situ ellipsometric measurements were performed at both the fundamental and SH frequency of the SHG experiment, to accurately characterize the linear optical parameters involved. All four measurements (SHG, linear reflectivity and ellipsometry at two wavelengths) are simultaneously fitted by a three-layer model as described in Ref. [10,11], with the etching speed as the only adjustable parameter. As expected, for thick oxides everything is governed by multiple reflections in the oxide film. Abrupt signal changes in the last few nanometers indicate changes...
in the interface region prior to the complete removal of the oxide.

2. Theory

For a (111) surface of a cubic crystal, the s-polarized SHG signal under s-polarized excitation can effectively be characterized by a single response parameter $\chi_{xxx}$ of the $\chi^{(2)}$ tensor [10,11]. The observed intensity $I_{s,s}$ can then be written as

$$I_{s,s} = |L_{2\omega} \chi_{xxx} \sin(3\Phi)|^2 I_{\omega}^2,$$

(1)

where $L_\omega$ and $L_{2\omega}$ are the Fresnel factors for the fundamental and SH frequency respectively, and $\Phi$ is the azimuthal angle. The dependence of $I_{s,s}$ on oxide thickness, angle of incidence etc., is governed by these Fresnel factors, which can easily be calculated [12], given the frequency-dependent optical constants of Si [17] and SiO$_2$ [18]. In an ellipsometry experiment one measures the ellipticity of the light reflected from a surface. This can be expressed in terms of the ratio of the complex reflection coefficients for s- ($r_s$) and p-polarized ($r_p$) light, and related to two ellipsometric angles $\Psi$ and $\Delta$ [19]:

$$\frac{r_p}{r_s} = \tan(\Psi) e^{i\Delta}.$$

(2)

Given the optical constants of the three-layer system the ellipsometric angles $\Psi$ and $\Delta$ and the linear reflectivity $R$ can also be calculated [19]. In this way, all four measurements can be described with one model, with the oxide thickness (or etching speed) as the only variable parameter. For the SHG signal and the reflectivity $R$ only an intensity scaling factor is added for the fitting.

3. Experiment

The samples are low-doped ($\sim 5 \times 10^{15}$ cm$^{-3}$) p-type Si(111) wafers (miscut < 0.5°), with a high-quality 300 nm thick thermal oxide. For the etching experiment a teflon cell was used, with a number of replaceable high-quality suprasil quartz windows, thereby accommodating angles of incidence of $\sim 4°$, $15°$, $30°$, $45°$, $60°$ and $75°$. The etch fluid was constantly stirred in order to get even etching and immediate removal of etched material from the surface of the sample. The same goes for the quartz windows which were also etched during the run of an experiment. Extensive testing however showed no roughening of the windows, and transmission measurements in the UV-VIS range showed no change in the transmission prior to and after a typical SHG etching experiment. If in doubt, windows were replaced. A thermostat bath was used to keep the temperature of the etch fluid constant within $0.1°C$. The temperature was recorded with a teflon-coated thermocouple placed in the etch fluid. A commercially available buffered NH$_4$F etch solution was used, with modified pH to obtain etching speeds of 1–2 nm/min. at $\sim 15°C$. Transmission experiments in the 200–900 nm range showed that the etch fluid was equally transparent as distilled water, and therefore the imaginary part of the refractive index of the etch fluid was assumed to be zero for the wavelengths used. The real part was measured by single-wavelength ellipsometry at 632.8 nm, and this was extrapolated to the relevant wavelengths using a Cauchy fit and interpolation with the well-known refractive index of water. For a given temperature the etch speed was constant, i.e. no speed changes were found in etching different oxide thicknesses [10,11]. This allows to obtain the oxide thickness from the etching times. Typical duration of an experiment was three hours. The starting oxide thickness was measured by single-wavelength ellipsometry and after each measurement a test sample was inserted in the etch-cell for a known amount of time to calibrate and check the etching speed in situ.

For the SHG experiment the frequency-doubled output at 532 nm of a Q-switched Nd:YAG laser was used. The fluence of the 8 ns pulses was limited to 10 mJ in a 4 mm diameter spot, well below the damage threshold and stable within 2%. The SHG signal was recorded using appropriate filters, a monochromator, photomultiplier and a gated integrator. The amplitude of $I_{s,s}$ was measured at an angle of incidence of $\sim 4°$ on the sample, which was mounted on a teflon holder and oriented prior to the experiment using X-ray diffraction. Due to the dispersion of the etch fluid the generated SHG beam is not parallel to the reflected fundamental beam. Great care was taken in alignment and the angle that was needed to rotate from the fundamental beam to the
SHG signal was consistent with the change in refractive index of the etch fluid, as obtained above. The linear reflectivity at a 60° angle of incidence was measured simultaneously using a green HeNe laser at 543 nm. This gave an in situ check of the multiple reflections which govern the thick oxide range of the measurement. The experiment was repeated under identical conditions and using samples cut from the same wafer, with a standard rotating-analyzer ellipsometer for both the fundamental (532 nm) and SH wavelength (266 nm) used in the SHG experiment, at an angle of incidence of 75°.

4. Results and discussion

Fig. 1 shows the results of all four measurements as a function of the oxide thickness. The points are the measurements and the solid lines the fits to be discussed below. The top trace is the SHG signal \( I_{sw} \), which is simultaneously measured with the linear reflectivity at 543 nm, which is shown in the second trace. The other two figures represent the measured ellipsometric angles \( \Psi \) and \( \Delta \) for 266 and 532 nm. It should be stressed that in total there are only three separate etching measurements (SHG + linear reflectivity, ellipsometry at 266 and 532 nm), all under identical conditions, and measured on three samples cut from the same wafer.

All four measurements show clear oscillations, due to the multiple reflections in the oxide film. The linear reflectivity and ellipsometry experiments show constant signal after the silicon is etched clean, as expected for a surface that is not changing in time or is in (dynamic) equilibrium with the etch fluid. It is well-known that these buffered NH\(_4\)F etch solutions yield a H-terminated silicon surface \[20\]. In contrast to the linear optical measurements, the SHG signal shows a drastic decrease when the silicon is etched clean. After this the signal remains constant for some time. Using the above mentioned model we fitted all four measurements. The optical constants of Si and SiO\(_2\) were taken from literature, the angle of incidences and the start thicknesses were put in but not fitted, and only the etch rates (one for each of the three independent measurements) and two scaling factors for the linear reflectivity and SHG experiment were fitted. The etch speeds fitted from the multiple reflections agreed well with the measured ones. As can be seen in Fig. 1, all the measurements are very well described by the model.

The key idea of this paper is to use the well-known thick-oxide region with the multiple reflections to see if there are any deviations from this model in the region of the very thin oxide thicknesses, possibly indicating transition layers, strain relief or other interface effects. The most obvious deviation is of course in the SHG experiment, where instead of reaching a constant value the signal decreases drastically when the silicon is etched clean. Lower SHG signals from H-terminated Si compared to oxidized Si have been observed by various authors \[6,8,21–25\], and is believed to come from two effects. First, the smaller electronegativity of hydrogen leads to a smaller nonlinear polarizability of the Si–H bond compared to the Si–O bond. Secondly, at the Si–SiO\(_2\) interface the Si is strained, leading to a loss of inversion symmetry in a thin layer of Si near the interface, where the SHG originates \[13–16\]. Hydrogen termination relieves this strain \[26\], thereby restoring inversion symmetry in the Si except for the top layer. This would also lead to a reduction of the SHG signal. Just prior to the large decrease of the SHG signal a small peak is observed with an amplitude of \( \sim 2 \) times the noise level, which has also been observed in other in situ SHG etching experiments \[23–25\]. Coinciding with this, very small but reproducible dips were observed in the ellipsometric angle \( \Delta \). These have also been observed in other in situ ellipsometric etching experiments, and explained in terms of the etching of a SiO\(_x\) \( (0 < x < 2) \) transition layer \[27\], or the formation of a hydrogen layer on the silicon surface \[28\]. All these effects cannot be explained within the simple three-phase model (ambient–SiO\(_2\)–Si) with ideal sharp interfaces, and using literature optical constants. In order to understand these microscopic details we feel it is essential to use these different linear and nonlinear optical techniques and one model to describe the measurements, using a minimum of free parameters and demanding consistency between the different methods. Such detailed studies for the last few nanometers are planned.
Fig. 1. Results of in situ optical measurements on the etching of SiO$_2$ films. SHG for 532 fundamental wavelength (top trace), linear reflectivity using a HeNe laser at 543 nm (second trace), ellipsometric angles $\Psi$ and $\Delta$ for 266 nm (third set of traces) and 532 nm (fourth set of traces). The points are the measurements and the lines are fits to the model described in the text, using only etching speed as fitting parameter.
5. Conclusions

We have performed in situ SHG, linear reflectivity and ellipsometric measurements to study the etching process of SiO$_2$ films. It was shown that one simple model describes all measurements very good, with only a minimum of free parameters. In contrast to the linear measurements the SHG signal shows a very high interface sensitivity and a large decrease in signal when the silicon is etched clean, which is explained with simple arguments. This also shows that SHG could be a useful indicator of etch-stop mechanisms.

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