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Citation for published version (APA):

Kroesen, G. M. W., Oehrlein, G. S., Frésart, de, E., & Haverlag, M. (1993). Depth profiling of the Ge concentration in SiGe alloys using in situ ellipsometry during reactive-ion etching. *Journal of Applied Physics*, 73(12), 8017-8026. <https://doi.org/10.1063/1.353916>

DOI:

[10.1063/1.353916](https://doi.org/10.1063/1.353916)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Depth profiling of the Ge concentration in SiGe alloys using *in situ* ellipsometry during reactive-ion etching

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(Received 20 March 1992; accepted for publication 11 January 1993)

The complex refractive index of SiGe alloys at 632.8 nm has been measured as a function of the Ge concentration using *in situ* ellipsometry while the material is slowly removed from a silicon substrate using reactive-ion etching (RIE). Homogeneous, strained epitaxial SiGe films on silicon substrates were used. The Ge concentration was obtained by Rutherford backscattering. If an unknown SiGe structure is etched with RIE, *in situ* ellipsometry yields combinations of the ellipsometric angles Ψ and Δ with time. Starting at the Si substrate, these points are, on a point-to-point basis, converted into combinations of complex refractive index and depth in a numerical procedure. For this inversion of the ellipsometry equations, the known relation between the real and the imaginary part of the refractive index of SiGe is used. Finally the refractive indices are converted into Ge concentrations. Thus the depth profile of the Ge concentration in an unknown epitaxial SiGe structure can be inferred from an *in situ* ellipsometric measurement during RIE of the unknown structure. The obtained resolutions in depth and Ge concentration are 0.3 nm and 0.3%, respectively.

I. INTRODUCTION

Recently alloys of silicon and germanium have been studied a great deal for possible use in high-speed device and optoelectronics applications.^{1,2} Devices made with strained epitaxial films of this material can be much faster than devices that exclusively use silicon.² The films may be grown by molecular-beam epitaxy (MBE) or by ultra-high-vacuum chemical-vapor deposition (UHVCVD).³ It is desirable to develop a routine method for determining the depth profile of the Ge concentration in a grown film. A number of techniques are available for that purpose. Among the nondestructive techniques, Rutherford backscattering spectrometry (RBS) is one of the most widespread. The depth resolution of that technique (about 50 nm), however, is not sufficient. Optical methods such as spectroscopic ellipsometry and IR reflection/absorption spectroscopy, with or without Kramers-Kronig analysis, can yield valuable information on the depth structure of the Ge concentration; however, when using these methods to obtain quantitative information in terms of Ge concentration depth profiles, one has to assume a certain model Ge depth profile of which the parameters can be obtained by fitting the results of the simulations using the model profile to the measured data: A direct, unambiguous interpretation of the measurement data is usually not possible. Among the destructive techniques able to provide the desired depth resolution the most widely used technique is secondary-ion-mass spectroscopy (SIMS). This method has two drawbacks, namely the size and the cost of the apparatus are substantial, and, since sputtering by energetic ions (~ 5 keV) is used to gradually remove the film

material, the roughening of the surface limits the depth resolution to about 5 nm (worst case) for routine measurements.

In this article we present an easily implemented (destructive) method that is able to provide the Ge concentration of the SiGe alloy at the desired depth resolution. The gradual removal of the material to be analyzed is done by RIE. *In situ* ellipsometry is used to determine the optical parameters of surface of the SiGe structure as it is etched. Since ellipsometry is not sensitive to emission or absorption of light by the plasma, it is one of the few surface techniques that is compatible with a plasma environment.

For an accurate depth profiling of the Ge concentration, detailed knowledge of the dependence of the refractive index of the SiGe alloy as a function of the Ge concentration is required. A complication is that the films are strained and epitaxial, with hardly any defects. This special type of material may possess optical constants that are different from those at the fully relaxed material.⁴ The references in the literature that do discuss the optical parameters of the material⁵⁻¹¹ do not provide the desired accuracy. Furthermore, they are all dealing with fully relaxed material. Therefore, an accurate determination of the complex refractive index of the material as a function of Ge content is necessary. To this end, we have performed *in situ* ellipsometry measurements while etching through homogeneous, comparatively thick SiGe films of a known Ge content. The film thickness cannot exceed a maximum value which depends on the Ge content. Films thicker than this maximum value contain many defects, and they will be partially relaxed. The Ge concentration has been calibrated with RBS. RBS directly yields the total Ge "dose" present on the surface. With the film thickness, which was determined using transmission electron microscopy (TEM), and the known material number density (since the film is epitaxial on silicon, the number density is the same as in

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silicon crystals), this determines the Ge concentration. An accurate analysis of the data provided by the ellipsometer now yields the desired complex refractive index.

The present article has two goals: first, the determination of the dependence of the complex refractive index of SiGe alloys on the Ge concentration, and second, the demonstration of the application of *in situ* ellipsometry during RIE for depth profiling of the Ge content. In the following we first discuss the experimental setup. Then the numerical algorithm which is used to interpret the direct results of the ellipsometer in terms of optical parameters is described. After that, the calibration of the system, necessary to eliminate the influence of interfering physical phenomena, is discussed and, finally, some results are shown.

II. EXPERIMENT

The experiments were done in a reactor equipped with a 12 in. water-cooled, quartz-covered rf-powered (13.56 MHz) electrode. The CF_4 gas was fed through a MKS mass flow controller. The flow rate was kept at 100 sccm at all times. A throttle valve in the pumping line to a 500 ℓ/s Leybold turbomolecular pump kept the pressure at 25 mTorr in all experiments. The wafer was placed on the powered electrode. The power used for the reported experiments varied between 10 and 400 W.

The reactor is capable of working in the RIE (reactive-ion etching) mode and also in the plasma etching mode. In the latter case the pressure is raised and the wafer is mounted on the grounded electrode. For the experiments reported in this article we have exclusively used the RIE mode, but we kept the power at a comparatively low level. When the power is raised, the flux and energy of the ion bombardment go up. This in turn causes a more profound modification of the etched surface, e.g., due to roughening or amorphization. In the plasma-etching mode the passivation layer that is formed on the surface¹² is likely to be thicker than in the case of RIE. In order to keep the impact of the plasma on the surface properties of the etched sample as low as possible, the low-power RIE conditions are preferred. Under these conditions the etch rate can be very low, e.g., about 0.05 nm/s. Since the measuring speed of the ellipsometer is limited (in our case about one measurement per second), a low etch rate implies a high depth resolution (if the intrinsic precision of the ellipsometer is better than the thickness of the material etched away between two data points).

The ellipsometer used in these experiments is an automated rotating compensator ellipsometer in the polarizer-sample-compensator-analyzer (PSCA) configuration.¹³ The polarizer is a Rochon prism, the analyzer a Glan-Thomson prism. A He-Ne laser is used as a light source, and a photomultiplier tube as a detector. In order to minimize the influence of the detection system on the measurement, the light passes a depolarizing diffuser located immediately behind the analyzer. An optical fiber transports the light to the photomultiplier. The signal of the photomultiplier is sampled 256 times each rotation of the compensator. The required trigger signals as well as an index pulse are supplied by an optical encoder, mounted on

the shaft of the rotating compensator. The compensator is unsupported mica. The data are taken by a 16 bit analog-to-digital converter (ADC), located in an Analog Device RT1850 interface card in an IBM PC/AT. The computer also performs the Fourier transform of the data, which is necessary to extract the ellipsometric angles Ψ and Δ .¹³ The minimum time between two measurements is 0.5 s. The instrument has a precision of about 0.01° in Ψ and in Δ . The principle of a rotating compensator, instead of a rotating analyzer, offers, among others, the advantage of a nonambiguous determination of Δ , with approximately the same precision for all Δ values. The angle of incidence was chosen between 74.0° and 75.0° . This range was chosen because it offers a good compromise between surface sensitivity and stability (which will be discussed more extensively later). The SiGe layers have been grown on 125-mm-diam Si(100) wafers by the UHV/CVD (ultra-high-vacuum/chemical-vapor-deposition) technique. The system is equipped with two hot-wall horizontal quartz reactors, with load-lock and transfer chambers.³ The base pressure in the reactors is 2.5×10^{-9} Torr at 550°C . Prior to loading the cassette in the system, the wafers were cleaned with a modified RCA procedure, then dipped in a 10% HF solution for 10 s. A gas mixture of pure silane and of germane (9.4%/He) was used for the deposition. The silane flow rate was kept constant at 14.2 sccm, corresponding to a partial pressure of 1.3 mTorr. The growth temperature was 518°C , as probed by a profile thermocouple located inside the reactor. These growth conditions, similar to the ones used by Meyerson, Uram, and LeGoues,¹⁴ provide excellent epitaxial quality.

III. NUMERICAL ALGORITHM

In the literature¹⁵ the procedure to calculate the optical parameters of a sample consisting of a substrate and several layers on it is described extensively. Essentially the Fresnel coefficients of all interfaces are calculated and all internal reflections in all films are added. Matrix methods, pioneered by Abelès,¹⁶ are applied to combine the several layers. A well-known program written by McCrackin¹⁷ is used to perform this calculation; however, if one wants to use the McCrackin program to analyze the measurements described in this article, one is forced to run the complete program for each datum. Therefore, we have used an approach that is similar to the McCrackin program, but with the advantages that (i) it allows us to start the simulation (if necessary) during the measurement, (ii) it allows for point-to-point analysis, i.e., interpreting the differences between two subsequent experimental points as an addition of a thin layer with a certain refractive index, and (iii) it allows the film thickness to assume negative values, thus facilitating the simulation of an etching process.

First a remark on the notation of the physical quantities in this article. Almost all relevant quantities (refractive indices n , impedance factors g , reflectance ratios r , angles ϕ , and even thicknesses d) are complex quantities (explanation later). In the following only one noncomplex quantity (the wavelength λ) occurs. Therefore, we have chosen

FIG. 1. Reflection of light at a stratified structure. The multiple internal reflections in the film material will interfere. Medium 0 is the ambient, medium 1 the substrate, and medium 2 the film material. The p, s coordinate system is taken left-handed for mathematical convenience.

not to change the typeface of the physical quantities: all of them (except the wavelength) are complex.

In order to cast the two Fresnel equations for polarization parallel p and perpendicular s to the plane of incidence into a mathematically very similar appearance, a left-handed coordinate system is used to represent the p and s directions. In that coordinate system the Fresnel equations become

$$r_p = \frac{n_1 \cos \phi_0 - n_0 \cos \phi_1}{n_1 \cos \phi_0 + n_0 \cos \phi_1}, \quad (1)$$

$$r_s = \frac{n_1 \cos \phi_1 - n_0 \cos \phi_0}{n_1 \cos \phi_0 + n_0 \cos \phi_1}. \quad (2)$$

Note that the left-handedness of the coordinate system has resulted in a sign change of r_s with respect to the convention in the literature.¹⁵ Figure 1 shows the multiple reflections in the film, and illustrates the numbering of the several media: ambient, substrate, and film(s). The plane of incidence coincides with the paper plane. The p direction is pointing into the paper plane, the s direction lies in the paper plane, and is perpendicular to the light beam, pointing away from the surface in the ambient. The impedance factors g_{pi} and g_{si} of a medium i are defined as

$$g_{pi} = \frac{n_i}{\cos \phi_i} = \frac{n_i^2}{\sqrt{n_i^2 - n_0^2 \sin^2 \phi_0}}, \quad (3)$$

$$g_{si} = n_i \cos \phi_i = \sqrt{n_i^2 - n_0^2 \sin^2 \phi_0}. \quad (4)$$

The Fresnel equations can be rewritten as

$$r_p = \frac{g_{p1} - g_{p0}}{g_{p1} + g_{p0}}, \quad r_s = \frac{g_{s1} - g_{s0}}{g_{s1} + g_{s0}}. \quad (5)$$

The mathematical appearances of r_p and r_s are now identical. If the surface is covered by a film, the phase thickness of the film is defined by

$$\beta_i = (2\pi d_i n_i \cos \phi_i) / \lambda = g_{si} 2\pi d_i / \lambda. \quad (6)$$

If now the complete system of substrate (medium 1) and film (medium 2) is looked upon as a new, semi-infinite substrate (medium x) with impedance factors g_x (the subscripts s and p will be omitted in the following), and if the internal reflections in the film are added, then

$$g_x = g_2 [(1+u)/(1-u)], \quad (7)$$

where

$$u = (g_1 - g_2) / (g_1 + g_2) \exp(-2j\beta_2). \quad (8)$$

If more films are present, this procedure can be repeated for each film, starting with the first one that contacts the semi-infinite substrate. From the impedance factors g_x the reflection ratio for waves incident from the ambient (medium 0) can be calculated by

$$r_{0x} = (g_x - g_0) / (g_x + g_0). \quad (9)$$

In order to return the end result to the conventional right-handed coordinate system, the ellipsometric angles Ψ and Δ and the complex reflection ratio ρ are defined by

$$\rho = \tan \Psi \exp(j\Delta) = -r_p / r_s. \quad (10)$$

The algorithm is also capable of taking into account an anisotropy in the refractive index, i.e., when the index has different values for waves travelling parallel or perpendicularly to the surface (p and s , respectively). Equations (3)–(6) then take a slightly different form, which is given in Appendix A.

It is possible to invert Eqs. (1)–(10) partially: When the impedance factors of the substrate and the film, as well as the complex reflection ratio ρ of the total system (substrate+film) are known, the film thickness can be calculated: let X be defined by

$$X = \exp(-2j\beta_2), \quad (11)$$

then X will be one of the two roots from the complex quadratic equation

$$AX^2 + BX + C = 0. \quad (12)$$

The coefficients A , B , and C depend on g_{s1} , g_{p1} , g_{s0} , g_{p0} , g_{s2} , g_{p2} and the reflection ratio ρ of the total system. The complete expressions are given in Appendix B. Since film thickness is normally a real number, not a complex one, the root with the smaller imaginary part is the physically relevant root. The magnitude of the imaginary part indicates the possible error of the calculated thickness (for the given optical parameters). The task of an interpretation routine for ellipsometric measurements is now to find the refractive index of the film material that gives the smallest (near-zero) error (imaginary part of the calculated thickness).

Note that the inversion procedure described here is more general than the inversion presented in the book of Azzam and Bashara¹⁵ or in the McCrackin program.¹⁷ Those inversions are based on the refractive index of the substrate, whereas the inversion described above is based on the impedance factors g_{p1} and g_{s1} of the substrate. The essential difference is that the "classical" method always has to start from a real, semi-infinite substrate. When one performs a point-to-point analysis of a Ψ - Δ contour, the

locally used "substrate" is in reality a stratified structure, consisting of the semi-infinite "real" substrate, covered with several films. Since the reflection and transmission ratios of a total system (local "substrate" plus film) depend not only on the complex reflectance ratio of the "substrate," but also on the absolute value of r_p , it is in general not allowed to assign an "effective refractive index" to the local "substrate" based upon the values of Ψ and Δ of that local "substrate." In other words: In general, a point-to-point analysis is not possible with the McCrackin program. The condition necessary to be able to use the classic inversion procedure in a point-to-point analysis is that the absolute value of r_p is known. This condition is met when the substrate is a semi-infinite medium, and also when the optical parameters of film and substrate differ only slightly.

It is possible to calculate the impedance factors of a substrate if the impedance factors of the total system (substrate+film) and of the film are known. This is simply done by following the algorithm for "adding" a layer to the system, while substituting a negative value for the film thickness. One can prove that the impedance factors of a substrate do not change if first a film is "added" to the substrate, and subsequently the same film is "subtracted" from the substrate by "adding" the same film, but with the sign of the film thickness changed. The mathematical proof is given in appendix C.

To conclude this section, we want to point out that the impedance factors g_s and g_p are not equivalent to the ellipsometric angles Ψ and Δ , nor to the "effective refractive index" of the total system. The impedance factors g_s and g_p correspond directly to the two reflection coefficients r_s and r_p [see Eq. (5)], whereas Ψ and Δ , as well as the effective index, are only related to the ratio ρ of r_s and r_p [see Eq. (10)]. Therefore, it is always possible to calculate Ψ and Δ from the impedance factors [Eqs. (5) and (10): only the ratio is needed] but (in general) not the other way round: It is not possible to "convert" Ψ and Δ into impedance factors unambiguously. The only exception is the semi-infinite medium (as stated before). Fortunately the Ψ - Δ to g conversion is not needed: in general, when calculating a multilayer system, one will use the impedance factors from the beginning at the substrate all the way to the top of the stack of layers; only then will the impedance factors of the whole system be converted to Ψ and Δ in order to allow for a comparison with measured Ψ - Δ data.

IV. CALIBRATION

Since the expected variations of the ellipsometric angles Ψ and Δ are not very large (a few degrees), instrumental errors and interfering physical effects might strongly affect the measurements and their interpretation. Possible external causes for errors are (a) deviations induced in the ellipsometer electronic signal processing unit by interference of the rf fields; (b) offsets introduced by the plasma light emission; (c) a shift in Δ due to the birefringence of the windows through which the laser beam enters and leaves the RIE chamber; (d) change of the angle of incidence due to a movement of the wafer induced by the electrical field or the pressure wave evoked by the ignition

of the plasma; (e) roughening, amorphization, and fluorination of the etched surface; (f) initial etching of the native oxide; (g) heating of the wafer by the plasma. In the following all these possible deviations will be addressed. Items (a) and (b) have been checked by performing several additional experiments.

A. rf interference

The influence of interference of the rf fields on the ellipsometer readings was checked by switching on another identical RIE reactor, which was in the same laboratory room, close to the one used for the experiments reported in this article. The ellipsometer signal was monitored on an oscilloscope. The magnitude of the rf interference was made equal for both RIE reactors in operation by tuning the power supplied to the second reactor. Separate switch-on and switch-off of the second reactor did not cause any change of the ellipsometer readings. As the ellipsometer signal processing uses Fourier transform, which is in this case only sensitive to the second and fourth harmonics of the rotation frequency of the analyzer, it is quite understandable that a high frequency, not phase related to the mentioned harmonics, does not cause any errors.

B. Plasma emission

The influence of the (visible) light emitted by the plasma was checked by placing a narrow-band interference filter between the analyzer and the detector. This filter eliminates all plasma radiation with wavelengths other than 632.8 nm. Since it is placed behind the analyzer, the polarizing properties of the filter do not influence the ellipsometer accuracy. The absence or presence of this filter did not have any influence at all on the ellipsometer readings. Since the ellipsometer data reduction scheme we applied does not use the dc component of the signal, but derives Ψ and Δ from the second and fourth harmonics of the compensator rotation frequency only, and since the light emitted by the plasma is not expected to be polarized, this insensitivity is quite understandable. We can conclude that neither rf interference nor plasma emission have any influence on the ellipsometer reading.

C. Window birefringence

It is always possible that the windows through which the laser beam enters and leaves the vacuum chamber show birefringence. This birefringence can be spontaneous, stress induced, or it might be caused by surface modification of the window material by contact with reactive species produced in the plasma. The shift in Δ , which is the result of window birefringence, may depend on the exact location where the laser beam passes through the window. It would be possible to determine the birefringence by taking measurements with and without the windows being present. Separate experiments have shown that indeed a small birefringence is measured. It is not practical, however, to remove and attach the windows after each sample change. Furthermore, the evacuation of the vacuum chamber causes the electrode to move slightly, which in its turn

FIG. 2. The evolution with time of the ellipsometric angle Ψ of a silicon surface covered with native oxide as the plasma is switched on and off. The parameter is the rf power level.

slightly changes the exact location where the laser beam crosses the window. Since the birefringence will be nonuniform over the window, one needs a calibration routine which does not involve removing of the windows and which can be carried out with an evacuated chamber.

The items (d), (e), (f) and (g) (wafer movement, surface modification, native oxide etching, and wafer heating, respectively) have been checked by performing *in situ* ellipsometry measurements on a Si wafer. Figures 2 and 3 show the change of the ellipsometric angles Ψ and Δ as a function of time while the plasma is switched on and off. The gradual, asymptotical change observed in both Ψ and Δ for high power levels (200 W) is caused by changing of the refractive index of Si caused by a temperature change of the wafer. This effect has been studied more extensively in a previous article.¹⁸ Since the temperature dependence of the refractive index of SiGe alloys is not known yet, one has to make sure that the effects of heating of the wafer by

FIG. 3. The evolution with time of the ellipsometric angle Δ of a silicon surface covered with native oxide as the plasma is switched on and off. The parameter is the rf power level.

FIG. 4. The ellipsometric angle Ψ as a function of film thickness for two refractive indices. In both cases the films are on a silicon substrate. The simulations were done at an angle of incidence of 74.0° , a value typical for the measurements presented in this article. The solid curve represents a refractive index of $1.48 - 0.003i$, a value reported for fluorocarbon residues of etch plasmas. The dashed curve represents a refractive index of $3.86 - 0.74i$, a value reported for amorphized silicon.

the plasma are negligibly small. Therefore low (< 100 W) power levels will have to be used.

The rapid initial changes in Figs. 2 and 3 are associated with the native oxide etching and the surface modification (damaging or amorphization and establishment of a fluorocarbon reaction layer). In order to be able to present a complete interpretation of the changes observed in Figs. 2 and 3, we will first investigate the influence of a modified surface layer by studying simulations which were carried out for the presence of an amorphized film on top of the silicon, and for a film with a refractive index of $1.48 - 0.003i$, the index found for fluorocarbon films created by a low-power fluorocarbon plasma.¹⁹ The refractive index of amorphized silicon at 632.6 nm is $3.88 - 0.76i$.²⁰ Figures 4 and 5 show the angles Ψ and Δ as a function of the film

FIG. 5. The ellipsometric angle Δ as a function of film thickness for two refractive indices. In both cases the films are on a silicon substrate. The simulations were done at an angle of incidence of 74.0° , a value typical for the measurements presented in this article. The solid curve represents a refractive index of $1.48 - 0.003i$, a value reported for fluorocarbon residues of etch plasmas. The dashed curve represents a refractive index of $3.86 - 0.74i$, a value reported for amorphized silicon.

FIG. 6. Ψ as a function of the angle of incidence for two situations: a clean silicon surface (solid curve) and a silicon surface covered with a transparent film with a thickness of 1 nm (dashed curve).

thickness for the above-mentioned refractive indices, at an angle of incidence of 74° . The presence of a transparent film affects only Δ ; Ψ is unaffected in first order. In first order an amorphized layer changes Ψ , but also to a lesser degree Δ . The effect which the presence of a thin transparent film has on Ψ is only negligible for certain values of the angle of incidence. This is illustrated in Fig. 6. There Ψ is compared for two situations: with and without a 1-nm-thick transparent film on a silicon surface. One observes that the presence of the film only has negligible consequences for Ψ if the angle of incidence is smaller than 74° . Working at a proper angle of incidence (74°) in the case of a transparent film (reaction layer) on the surface, the effect of the presence of that film on the Ψ - Δ plots is equivalent to the effect of a (small) window birefringence: a mere Δ shift.¹⁵ This is once more illustrated in Fig. 7. Here two simulations are shown. Both correspond to the growth of a homogeneous SiGe film on Si. The starting point (Si semi-infinite substrate) is indicated. The refractive index of the SiGe film, the thickness increments, and the number of simulation points are arbitrary, but identical for the two shown figures. The difference is that the full curve corresponds to a "clean" system, whereas for the dashed curve there is a 1-nm-thick transparent film (reaction layer) sitting on top of the growing SiGe. The two curves are practically identical, except for a Δ shift. An amorphization of the surface changes Ψ as well as Δ , and therefore has to be avoided: A power level will have to be chosen that leaves the angle Ψ undisturbed. Looking at Fig. 2, for our conditions a power level of 50 W or lower will serve our goals in this respect. It is not expected that the amorphization of SiGe occurs at much lower power levels (read: ion bombardment energies) than in the case of Si. From the ellipsometry data we have never found any indications that this would be the case. The fast initial increase in Ψ observed for 200 W, and less pronounced at 100 W, may be caused by two effects: a change of the angle of incidence due to movement of the wafer induced by the ignition of the plasma or a quick amorphization of the surface. In the present reactor geometry the electrode construction does not allow the wafer to

FIG. 7. Two simulations of the growth of a homogeneous SiGe film on Si. The solid curve corresponds to the "clean" situation, the dashed curve to the presence of a 1-nm-thick reaction layer on top of the growing SiGe film.

be anchored: a change in the angle of incidence cannot be excluded completely. Since the effect is nonreversible, an amorphization is likely.

Figure 3 shows that Δ undergoes an initial rapid increase, followed by a rapid decrease. Then Δ tends toward an equilibrium value that differs from the initial value. For high power levels the extinction of the plasma induces an asymptotical behavior, attributed to temperature change. In the first two rapid changes two effects compete: the etching of the native oxide (causing an increase in Δ) and the modification (e.g., roughening, fluorination, formation of a fluorocarbon film) of the surface (generally causing a decrease in Δ). Figure 3 suggests that etching of the native oxide starts immediately after plasma ignition (Δ increase, $\Psi \sim \text{const}$). Shortly after that, the surface modification begins, causing a temporary decrease in Δ , quickly followed by an increase in Δ when the oxide etching takes over the leading role again. After a while, when all of the oxide is etched away, the situation becomes stable. The power level seems to mainly influence the time scale at which the oxide etching and the establishing of the surface fluorination occur. The asymptotic Δ increase corresponds (for 50, 100, and 200 W) to an oxide thickness of 13 Å. The effect of the mentioned phenomena on Δ is indistinguishable from the earlier-mentioned Δ shift caused by window birefringence. Therefore, the calibration routine that is necessary to correct for the window birefringence will also automatically "remove" the effect of the modified surface layer.

We can summarize the effects of external causes of error as follows: Ψ only changes when the angle of incidence changes, or when the surface amorphizes. The other effects, i.e., fluorocarbon deposition, surface roughening,

FIG. 8. The Ψ - Δ curve measured with the *in situ* ellipsometer during the reactive-ion etching of a homogeneous SiGe alloy on a silicon substrate. The points denote the measured values, the solid curve the simulation.

FIG. 9. The real part of the refractive index of strained epitaxial SiGe alloys as a function of the relative germanium concentration.

and window birefringence, cause mainly a shift in Δ . We therefore propose the following calibration routine. A power level of 50 W or lower will be used in order to minimize the influence of the surface modification on Ψ . During the profiling of a SiGe structure the measurement is continued until the Si substrate is reached and Δ and Ψ have become stationary. The refractive index of Si at 632.8 nm is well known ($3.88 - 0.019j$).²¹ The angle of incidence is now calculated from the Si refractive index and the Ψ value of the end point. After that, the Δ values of the complete measurement are shifted, the shift being determined by the difference between (a) the Δ value associated with the determined angle of incidence and the Si refractive index and (b) the measured Δ value of the end point. In this way the Δ shifts caused by the various mentioned effects (with possibly different signs) are eliminated.

V. RESULTS

The real and imaginary part of the refractive index of SiGe alloys were determined by performing *in situ* ellipsometry measurements during reactive ion etching of homogeneous thin films on Si. A typical example of a Ψ - Δ plot is given in Fig. 8. This measurement was taken during the etching of a homogeneous SiGe film on a silicon substrate. The end point of the measurement (the clustered points on the left-hand side) corresponds to the Si substrate. The simulation was obtained by increasing the thickness of a SiGe film on silicon; in fact, a time-reversed simulation of the etching process. The points denote the measurements, the full curve the simulation. The simulation was calculated using the algorithm described in Sec. III, assuming a single-layer etching model. Note that the possible effect of a surface modification has been "removed" from the measurement by the calibration described in Sec. IV (basically a Δ shift). This has been done to show the shape similarity of measurements and calculations. Ψ - Δ plots like these have been taken and analyzed for a number of Ge concentrations in the alloy. From those measurements the real and imaginary parts of the refractive index were determined as a function of the Ge con-

centration. In Fig. 9 the real part of the index of refraction of the strained epitaxial SiGe films is plotted versus the atomic germanium concentration. The points represent the experimental data, the full curve represents a least-squares polynomial fit. An adequate fit has been obtained with the following formula: $\text{Re}(n) = Ax^2 + Bx + C$, where $A = 1.0395 \times 10^{-4}$, $B = 3.3733 \times 10^{-3}$, and $C = 3.87972$. The imaginary part (Fig. 10) is in all cases roughly equal to -0.02 . As expected, the index approaches the silicon value for small Ge concentrations. In Figs. 9 and 10 the dashed curve corresponds to the results reported by Humlicek *et al.*⁵ for fully relaxed material. For the fully relaxed material the real part of the refractive index is consistently higher than for the strained material. The refractive index is determined by, on one hand, the product of density and atomic polarizability, and, on the other hand, by macroscopic phenomena such as strain. Relaxed material is less dense than epitaxial material (on Si); this would lead to a lower value of the refractive index for relaxed material. Since the measurements show that the index for relaxed

FIG. 10. The imaginary part of the refractive index of strained epitaxial SiGe alloys as a function of the germanium concentration.

FIG. 11. Transmission electron micrograph of the structure of the superlattice sample analyzed with *in situ* ellipsometry during RIE.

material is instead higher than for epitaxial material, one can conclude that the refractive index of strained, epitaxial SiGe films on Si is to a large extent determined by strain.

To demonstrate the capability of the interpretation algorithm presented in Sec. III to perform a point-to-point simulation, a superlattice structure containing several layers of SiGe with varying Ge concentration, intermitted with intrinsic Si, was etched and analyzed. The result is presented in the Figs. 11–14. Figure 11 shows a transmission electron micrograph (TEM) of the sample under study here. The interfaces appear to be very sharp, and the material is very homogeneous and defect free. Figure 12 presents the Ψ - Δ contour that has been measured while the film was etched using RIE (100 sccm CF_4 , 12 in. electrode, 25 mTorr, 50 W). In Fig. 12 the points represent the measured Ψ - Δ combinations, and the curve represents a simulation. The sharp bends of the Ψ - Δ curve when a new zone

FIG. 12. Ψ - Δ contour measured during RIE of the superlattice sample depicted in (a). The points represent the measurement values, the solid curves simulations. For clarity the simulations for each homogeneous depth range have been extended slightly to either side. The sharp edges that occur at the boundary between two different materials are obvious.

FIG. 13. Ellipsometrically determined depth profile of the germanium concentration in the superlattice structure under study.

of material is entered are very obvious. The measurements start on the right-hand side. The Si end point corresponds to the “end” of the string of measurement points in the center. That is also where the simulation is started. The simulation is roughly based on a stack of five layers of SiGe material, each about 60 nm thick, with refractive indices (see Figs. 9 and 10) corresponding to 2%, 5%, 7%, 11%, and 14% Ge, respectively (from bottom to top), which are alternated by silicon films of about 20 nm thick. For each layer of Si or SiGe the simulations have been extended longer than the thickness which is indicated by the measurements. They have also been extended in the “other” direction, using negative film thicknesses. In this way, in the simulation, a sudden change of the refractive index, which corresponds to a SiGe/Si transition, shows up as the crossing point of two curves. On the right-hand side there is a substantial difference between the measurements and the simulation, which is based on a homogeneous SiGe/Si superlattice. This indicates that the topmost SiGe film is not homogeneous.

FIG. 14. SIMS measurement of the depth profile of the relative germanium concentration.

If one knows in advance that the material is epitaxial SiGe, then the ellipsometric equations can be inverted. In that case the refractive index has to correspond to the curves in Figs. 9 and 10: The relation between real and imaginary parts of the refractive index is known. The ellipsometer yields two data: Ψ and Δ . In principle there are three unknowns: the real part of the refractive index, the imaginary part, and the thickness of the layer etched away between two data points. If the relation between real and imaginary part of the refractive index is used, the number of unknowns reduces to two. This system can be solved.

The interpretation of a Ψ - Δ contour is started at the Si end point, where at first the angle of incidence and the Δ shift are calibrated. Then all measurements are addressed in a time-reversed order. Starting from the impedance factors of a datum, the thickness (complex number) is calculated for an array of values of the refractive index of the film material corresponding to several Ge concentrations. The calculation uses the algorithm described in Sec. III and Appendix B. All results (values of the thickness) with a negative real part are rejected. For the results with a positive real part, a sign change of the imaginary part is searched for. Once the sign change has been located as to occur between two values of the Ge concentration (or rather, between the two values of the refractive index corresponding to two Ge concentrations), the exact position of the zero of the imaginary part is interpolated by the *regula falsi*.²² This method has the advantage over, for instance, the Newton-Raphson method that convergence is guaranteed. In this way, starting from the silicon substrate, from datum to datum two numbers are obtained: the thickness of the layer, and the location in the array of refractive index values, interpretable as the Ge concentration.

This procedure was applied to the Ψ - Δ plot displayed in Fig. 12, and the result, a plot of Ge concentration versus depth, is presented in Fig. 13. The depth is obtained by accumulating the thicknesses of the layers "inverted" by the algorithm. For comparison, Fig. 14 displays the SIMS depth profile for the same wafer. The two profiles are very similar. The ellipsometrically obtained profile shows more detail, and has a better depth resolution. Furthermore, there is no calibration required, other than the one performed in this article: the relation between the refractive index of the SiGe alloy and the Ge content. Both the depth scale and the concentration scale are absolute, where SIMS has to be calibrated along both axes.

VI. CONCLUSIONS

The complex refractive index at 632.8 nm of strained, epitaxial SiGe films on Si substrates has been determined as a function of the Ge concentration using *in situ* ellipsometry during reactive-ion etching. Using the now known relation between the real and imaginary part of the refractive index, the ellipsometric data can be inverted, yielding for each datum the thickness of the layer etched away between the taking of that datum and the taking of the previous one, and also the Ge concentration of that layer. In this way a depth profile of the Ge concentration in the investi-

gated sample can be obtained. The measurements have to be corrected for interfering physical phenomena like window birefringence, surface modification, and wafer movement during plasma ignition.

APPENDIX A: ANISOTROPIC MEDIA

The impedance factors g_s and g_p for an anisotropic medium are

$$g_s = n_s \cos \phi_s = \sqrt{n_s^2 - n_0^2 \sin^2 \phi_0}, \quad (\text{A1})$$

$$g_p = \frac{n_s}{\cos \phi_p} = \frac{n_p n_s}{\sqrt{n_p^2 - n_0^2 \sin^2 \phi_0}}. \quad (\text{A2})$$

Here n_p and n_s denote the refractive index of the medium for waves traveling in a direction parallel or perpendicular to the surface, respectively. The phase thickness β is now different for the p and s directions:

$$\beta_s = 2\pi g_s d / \lambda, \quad (\text{A3})$$

$$\beta_p = 2\pi n_s^2 d / (g_p \lambda). \quad (\text{A4})$$

APPENDIX B: COEFFICIENTS OF EQ. (12)

The coefficients of the quadratic equation (12) that yields the two possible values of the (complex) thickness of the film for given refractive indices of the film and of the ambient, and a given set of impedance factors for the substrate, are

$$A = c_s c_p [g_{s2} g_{p2} (\rho + 1) - g_{s2} g_{p0} (\rho - 1) + g_{p2} g_{s0} (\rho - 1) - g_{p0} g_{s0} (\rho + 1)], \quad (\text{B1})$$

$$B = (c_s + c_p) g_{s2} g_{p2} (\rho + 1) + (c_s - c_p) g_{s2} g_{p0} (\rho - 1) + (c_s - c_p) g_{p2} g_{s0} (\rho - 1) + (c_s + c_p) g_{p0} g_{s0} (\rho + 1), \quad (\text{B2})$$

$$C = g_{s2} g_{p2} (\rho + 1) + g_{s2} g_{p0} (\rho - 1) - g_{p2} g_{s0} (\rho - 1) - g_{p0} g_{s0} (\rho + 1). \quad (\text{B3})$$

Here

$$c_s = \frac{g_{s1} - g_{s2}}{g_{s1} + g_{s2}}, \quad c_p = \frac{g_{p1} - g_{p2}}{g_{p1} + g_{p2}}. \quad (\text{B4})$$

The two roots are given by

$$X_{1,2} = (-B \pm \sqrt{B^2 - 4AC}) / 2A. \quad (\text{B5})$$

APPENDIX C: VALIDITY OF NEGATIVE FILM THICKNESSES

Equations (6), (7), and (8) together yield the impedance factors for a total system of substrate (medium 1) and film (medium 2) with respect to an ambient (medium 0). Since the mathematical manipulations to follow are exactly the same for p and s polarizations, we will omit the s and p subscripts.

We will now calculate the impedance factors g'_x of the total system defined by Eqs. (6)–(8), but with a film

“added” which has the same refractive index n_2 as the film added in Eq. (7), but with a negative thickness $-d_z$. Analogous to Eqs. (6)–(8) we can write

$$g'_x = g_2[(1+u')/(1-u')], \quad (C1)$$

$$u' = [(g_x - g_2)/(g_x + g_2)] \exp(-2j\beta'_2), \quad (C2)$$

$$\beta'_2 = -\beta_2. \quad (C3)$$

We substitute Eq. (C2) into Eq. (C1):

$$g'_x = g_2 \frac{g_x + g_2 + (g_x - g_2) \exp(2j\beta_2)}{g_x + g_2 - (g_x - g_2) \exp(2j\beta_2)}, \quad (C4)$$

or

$$g'_x = g_2 \frac{g_x[1 + \exp(2j\beta_2)] + g_2[1 - \exp(2j\beta_2)]}{g_x[1 - \exp(2j\beta_2)] + g_2[1 + \exp(2j\beta_2)]}. \quad (C5)$$

After transformation of g_x from Eq. (7) analogous to the evolution of Eqs. (C1)–(C5), resulting in

$$g_x = g_2 \frac{g_1[1 + \exp(-2j\beta_2)] + g_2[1 - \exp(-2j\beta_2)]}{g_1[1 - \exp(-2j\beta_2)] + g_2[1 + \exp(-2j\beta_2)]} \\ = g_2 \frac{g_1[1 + \exp(2j\beta_2)] + g_2[\exp(2j\beta_2) - 1]}{g_1[\exp(2j\beta_2) - 1] + g_2[1 + \exp(2j\beta_2)]}, \quad (C6)$$

we substitute Eq. (C6) into Eq. (C5). After some calculation, the result is

$$g'_x = g_1. \quad (C7)$$

If the calculation is done the other way round, i.e., starting with the “removal” of a layer, followed by the “addition” of the same layer, the result is identical.

We have proven now that the “subtraction” of a layer from a surface with certain impedance factors g_x in effect yields the impedance factors of a surface that, when the subtracted film is added to that surface, yields the same impedance factors g_x . This is exactly what one needs for the simulation of an etching process.

This technique, calculating the optical parameters of a substrate when the optical parameters (i.e., the impedance

factors) of the total system and of the film are known, is in fact an inversion of the ellipsometric equations.

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