

Infrared ellipsometric study on the initial stages of oxide growth on Si(001)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S4335

(<http://iopscience.iop.org/0953-8984/16/39/008>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:56

Please note that [terms and conditions apply](#).

Infrared ellipsometric study on the initial stages of oxide growth on Si(001)

K Hinrichs¹, M Gensch¹, A Röseler² and N Esser¹

¹ ISAS, Institute for Analytical Sciences—Department Berlin, Albert-Einstein-Street 9, 12489 Berlin, Germany

² Gesellschaft zur Förderung der Angewandten Optik, Optoelektronik, Quantenelektronik und Spektroskopie eV, Rudower Chaussee 29, 12489 Berlin, Germany

Received 15 April 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/S4335

doi:10.1088/0953-8984/16/39/008

Abstract

The initial stages of native oxide growth on an etched Si(001) surface have been studied by infrared (IR) spectroscopic ellipsometry. The mid-infrared ellipsometric spectra show characteristic vibrational bands of Si–H stretching vibrations between 2100 and 2200 cm^{-1} , and bands of silicon oxide between 1000 and 1290 cm^{-1} . The most intense band in the range of Si–H stretching vibrations is assigned to a vibration of SiH_2 groups, while the most prominent bands from the oxide interface can be assigned to bands originating from different Si–O stretching vibrations. By monitoring these bands during degradation of the passivated surface in atmospheric conditions different steps of the oxide growth at the interface are identified. The frequencies of the Si–O bands differ from those in thicker films. It is concluded that at the very beginning the top Si atoms are oxidized by replacement of the hydrogen bonds allowing the subsequent oxidation of the back bonds.

1. Introduction

In order to improve the functionality of electronic devices, the growth mechanism, the chemical structure and the optical properties of thin SiO_2 layers on Si(001) have been intensively studied by theoretical [1–6] and experimental methods.

A variety of surface sensitive methods such as x-ray photoelectron spectroscopy (XPS) [7–9], high resolution electron energy loss spectroscopy (HREELS) [10], reflection high energy electron diffraction (RHEED) [11], scanning tunnelling microscopy (STM) [6, 12], x-ray reflectometry [13], reflectance anisotropy spectroscopy (RAS) [14], infrared reflection–absorption spectroscopy [15–18] and infrared-attenuated total reflection IR-ATR [19–21] were applied. Ellipsometry in the UV–VIS spectral range has evolved into a standard tool to determine the thickness of thin oxide layers [22, 23]. With the advent of commercially available

infrared ellipsometers, infrared spectroscopic ellipsometry has also been increasingly used [24–28] to study thin silicon oxide films. In this work we show that the sensitivity of IR-ellipsometry allows one to study even the very initial steps of oxide growth in a single reflection geometry. In comparison to visible ellipsometry in the infrared spectral range a high spectral contrast for structure analysis is achieved by direct observation of specific vibrational bands. The interpretation of the determined infrared ellipsometric parameters by optical modelling gives not only the thickness but often direct access to the molecular structure. For the investigation of the initial formation of the oxide film on silicon the latter molecular information is of particular interest.

The density of the amorphous oxide at the interface is expected to be different to that of vitreous silica [2]. According to the literature the interface is believed to consist of different suboxide structures [29]. Depending on the humidity of the air, periods of up to 150 days were found for the interfacial growth [11, 17]. In this work the oxidation of an etched Si(001) surface is studied over a period of 14 days by monitoring the bands from Si–O as well as Si–H stretching vibrations.

2. Experimental details

2.1. Preparation

The substrate used in this study was a Czochalski grown, Boron doped ($3 \Omega \text{ cm}$) Si(001) wafer (offcut $<1^\circ$). The wafer was prepared by a procedure according to [30]. Prior to etching the sample was cleaned with deionized water and ethanol. It was etched for 20 min in a solution of HF–H₂O–ethanol (1:1:10). Afterwards it was rinsed in ethanol in order to prevent an initial oxidation by water [30]. By this procedure a disordered smooth hydrogen passivated Si(001) surface is achieved.

2.2. Ellipsometry

The concept of the in-house-built photometric ellipsometer used in this study has been described in detail elsewhere [31, 32]. The ellipsometer is attached to a Bruker IFS 55 Fourier transform spectrometer. The ellipsometric parameters are derived from the ratio of intensities of single beam spectra measured for four different polariser positions (0° , 45° , 90° , 135°). A second set of measurements performed with a KSR5 retarder provides for the accurate determination of Δ for values of $|\cos \Delta| \sim 1$. A liquid nitrogen cooled mercury cadmium telluride (MCT) detector was used in all measurements.

2.3. Calculation

Spectral simulations of the ellipsometric spectra $\tan \Psi$ and Δ were carried out to determine the optical constants and thickness. The special optical model of an isotropic film on an isotropic substrate in isotropic ambient was used. The simulations within the optimization routines were simplified by employing the explicit analytical expressions for this optical model derived from the 4×4 matrix formalism and given by Azzam and Bashara [33]. The vibrational properties are included by modelling of molecular vibrations as harmonic oscillators with a damping constant Γ , a resonance frequency ν and an oscillator strength F . Details are described in [34].

3. Results

3.1. Ellipsometric measurement

Figure 1 shows the ellipsometric $\tan \Psi$ spectra in the spectral ranges from 930 to 1350 cm^{-1} and 2000 to 2250 cm^{-1} for different storage times in air starting from the H-passivated surface (top)

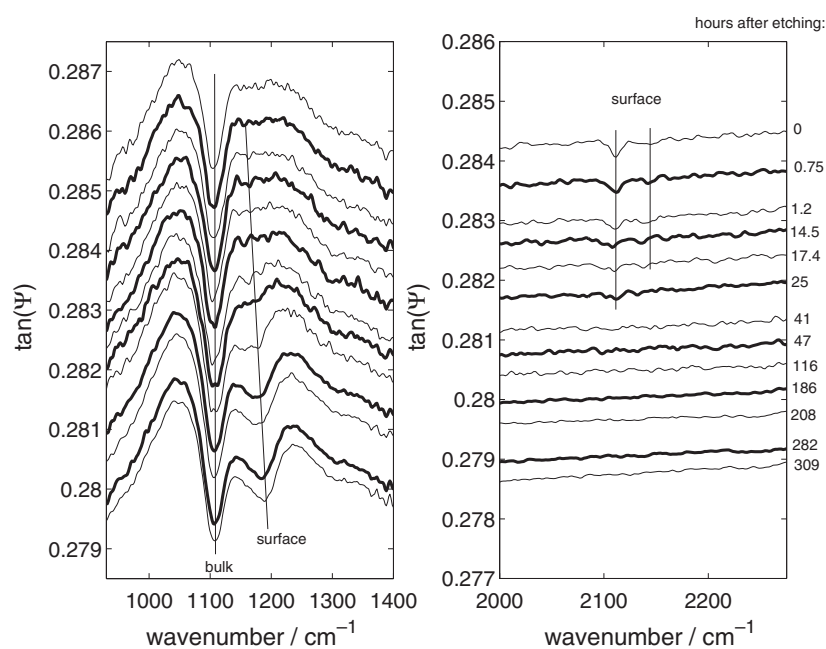


Figure 1. Ellipsometric spectra for different storage times in air at a spectral resolution of 4 cm^{-1} . The baseline of the spectra have been shifted by less than 0.006 for better representation. Surface and bulk related signals are marked. The band present in all spectra at around 1100 cm^{-1} is due to a low-energy anharmonic excitation (LEAE) of interstitial oxygen in the bulk of the silicon crystal [35, 46].

to an oxidized surface after two weeks (bottom). The frequency range from 930 to 1250 cm^{-1} is characteristic for Si–O–Si stretching vibrations. In this spectral region the surface related bands are overlapping with a broad band at around 1100 cm^{-1} . This band is assigned to an absorption of a low-energy anharmonic excitation (LEAE) of interstitial oxygen in the bulk of the silicon crystal [35, 46]. As a general criterion in the identification of real bands we used the Kramers–Kronig relation of real bands in $\tan\Psi$ and Δ spectra which is not likely for artefacts.

The range between 2000 and 2250 cm^{-1} is characteristic for H related stretching vibrations. A variety of bands originating from stretching vibrations of different hydrogen and oxygen terminated Si atoms have been observed in the frequency range between 2000 and 2300 cm^{-1} (e.g. for a Si(001) surface: SiH(O₃) [17, 20], SiH₂(O₂) [17], SiH₂ and SiH [17, 20]). In the following the Si–O and Si–H related spectral ranges are discussed in detail.

4. Discussion

4.1. Si(O_x)H_y stretching vibrations (2000 – 2250 cm^{-1})

As mentioned above, differently prepared hydrogen passivated Si(001) surfaces have been studied by various authors using infrared attenuated reflection [19–21], infrared reflection–absorption spectroscopy [15–18] and infrared ellipsometry [37].

Experimental and theoretical results have been used to discuss different models for the complex network of Si–H and Si–O bonds forming upon exposure to oxygen [1–6].

Figure 2 shows ellipsometric spectra for the initial steps of the oxidation in the frequency range from 2000 to 2275 cm^{-1} . The general behaviour of the ellipsometric spectra shown

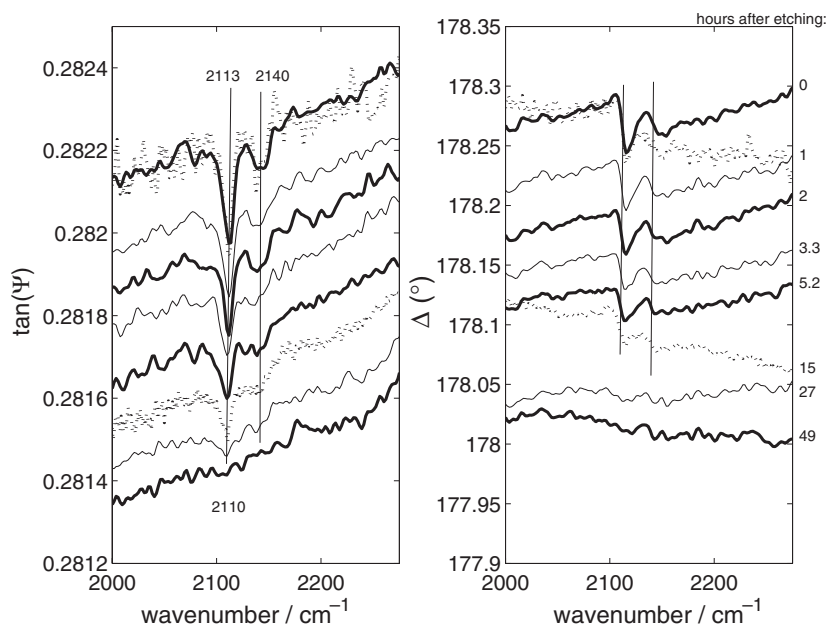


Figure 2. IR ellipsometric spectra taken directly after etching (top spectra) and after subsequent oxidation in air in the frequency range of the Si–H stretching vibrations. The time in hours when the measurement was started is given relative to the end of the etching process. The incidence angle was 65° . The spectra were recorded at a spectral resolution of 4 cm^{-1} (solid curves) and a resolution of 2 cm^{-1} (at 0 and 15 h after etching, dotted curves). The Kramers–Kronig correlated bands are marked by lines.

here were reproduced for several samples produced with the same etching procedure. Peaks around 2113 and 2140 cm^{-1} are identified as real bands because of their Kramers–Kronig correlation. It is generally observed that the band amplitudes decrease with the exposure time to air ($21 \pm 3\%$ relative humidity).

The amplitudes of the two bands decrease gradually, indicating a degradation of the hydrogen termination. The band that is initially observed at around 2113 cm^{-1} is shifting by about 3 cm^{-1} to lower wavenumbers upon exposure to air.

Spectra with a higher spectral resolution of 2 cm^{-1} have been recorded at selected exposure times in order to determine the shift of the resonance frequency more precisely. In figure 3 calculations for the ellipsometric parameters in an isotropic optical model for the Si–H film are compared to the ellipsometric measurement of the hydrogenated surface immediately after etching. A value of 0.5 nm was used for the thickness of the Si–H film. The value for the high frequency refractive index $n = 1.378$ was taken from [36]. The actual resonance frequencies (damping constants) for the bands were then determined to be at 2110 cm^{-1} (8 cm^{-1}) and 2138 cm^{-1} (16 cm^{-1}). The degradation of the hydrogen termination upon exposure to air was modelled by scaling the oscillator strength of the referring Si–H bands by factors of 1, 0.8, 0.6, 0.4, 0.2 and 0.

An overall agreement between the simulated and measured spectra is found, indicating that a layer model can be applied for the interpretation of ellipsometric spectra of an atomic layer. A similar approach was successfully applied in a previous work on H-passivated Si(111) [37]. By comparison with literature data (see table 1) the main band is assigned to the stretching vibration of the SiH_2 group. The assignment of the broad band around 2138 cm^{-1} is not unequivocal. It could either be due to SiH_x [12, 38, 39] or to $\text{SiH}_2(\text{O})$ [20] groups. However

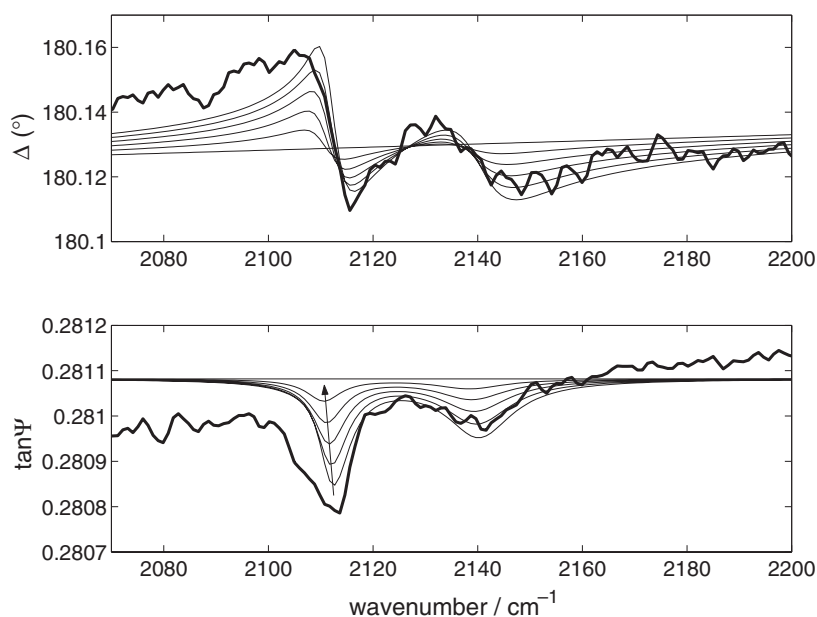


Figure 3. Ellipsometric spectrum recorded after etching with a spectral resolution of 2 cm^{-1} (thick solid curve) is shown in comparison to calculated spectra (thin solid curves) for successively reduced oscillator strengths (1, 0.8, 0.6, 0.4, 0.2, 0). The following input parameters were used in the calculation: $n_{\text{substrate}} = 3.59 + i \cdot 0.001$; $F_{2110} = 17\,000\text{ cm}^{-2}$, $F_{2138} = 14\,000\text{ cm}^{-2}$. Note that reflections from the rough backside of the substrate lead to a slight overestimation of the refractive index. The measured value Δ was shifted by 0.965° . This deviation is most likely caused by the nonlinearity of the MCT detector. The modulation of the background in the measured spectrum originates from interference fringes within the substrate.

Table 1. Frequencies of Si–H stretching vibrations as calculated from the measured ellipsometric spectra in comparison to those determined experimentally. *: assignment is discussed in the text.

Vibration	cm^{-1} (literature)	cm^{-1} (this work)
SiH	2080 [17], 2084 [12, 38]	
SiH ₂	2110 [17, 20, 40], 2103–2113 [12], 2104–2121 [38]	2110
SiH ₂ (O ₂)	2200 [17, 20]	
SiH(O ₃)	2250 [17], ~2248 [20]	
SiH ₃ (sym)	2123 [12], 2129–2145 [38]	
Constrained SiH ₂	2129–2145 [38]	
SiH ₂ (O)	~2148 [20]	2138*
SiH ₂ on steps of Si(111)	2137 [20]	

since its amplitude decreases monotonously (see figures 1–3) with the exposure time in air it is most likely not caused by SiH₂(O) groups. The band could be due to SiH and SiH₃ bonds at step edges or on [111] facets, indicating a considerable microscopic roughness of the interface according to [12]. Another possible explanation for the broad band is that it originates from lying Si–H bonds, where the force constants are enhanced due to stronger H–H interactions. It is expected for dihydrides on (1×1) Si(001) surfaces, to release the strong repulsive interactions between the H atoms of adjacent dihydrides by forming a canted dihydride structure with one Si–H band more parallel and the other one more perpendicular

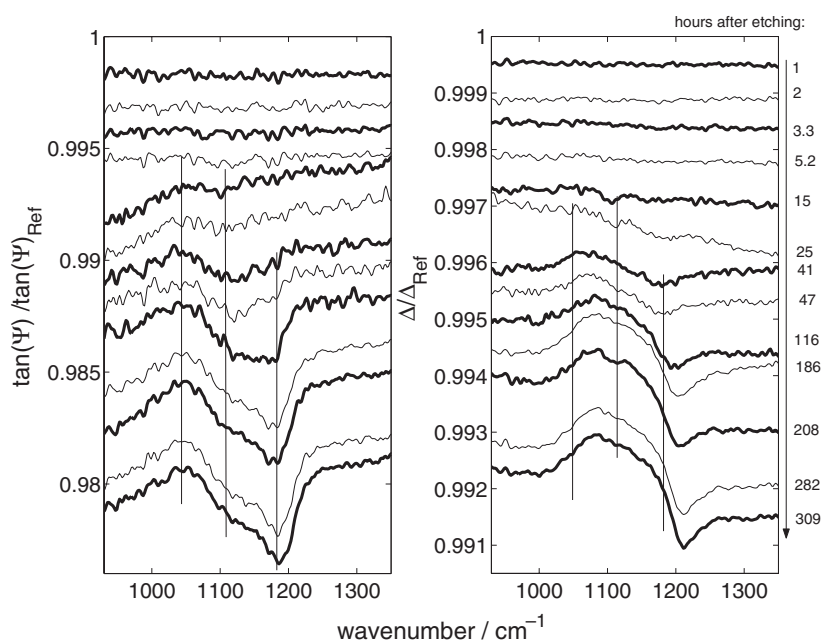


Figure 4. Ratios of $\Delta/\Delta_{\text{Ref}}$ and $\tan \Psi/\tan \Psi_{\text{Ref}}$. As reference spectra served the spectra of the H-passivated sample. Characteristic structures are marked.

to the surface plane. The resonance frequency of this band has been calculated by a first principles study [39] and a shift by $40\text{--}50\text{ cm}^{-1}$ is predicted with respect to upright standing Si–H vibrations. $\text{SiH}_2(\text{O}_2)$ or $\text{SiH}(\text{O}_3)$ related bands as observed in [17] have not been found, suggesting that no significant oxidation of back bonds occurs within the timescale of about 24 h, in agreement with [40].

The observed band shift of the Si–H band at around 2113 cm^{-1} with the duration of exposure to air is well reproduced in the calculation. It should be noted that the band frequency was kept constant at 2110 cm^{-1} in the calculation. The replacement of hydrogen by oxygen and referring decay of the Si–H bond density is modelled by simply lowering the oscillator strength. The frequency shift is here the result of an optical effect that is often referred to as the Berreman effect [41, 45].

4.2. Si–O–Si stretching vibrations ($930\text{--}1300\text{ cm}^{-1}$)

In infrared reflection, e.g. infrared ellipsometric spectra of thin silicon oxide films, typically two different types of bands are found [16–18, 24]. Bands due to the TO modes of the Si–O–Si stretching vibrations are commonly observed below 1100 cm^{-1} and exhibit a positive sign in the $\tan \Psi$ spectra. The more prominent bands in reflection spectra, often referred to as Berreman modes [41, 45], are found in the spectral range of the LO phonon modes and exhibit a negative sign in the $\tan \Psi$ spectra. The frequencies of these bands vary depending on the density and structure of the SiO_2 film. Generally a shift to longer wavelengths is observed for decreasing thicknesses [24, 29].

In figure 4 the ratios for $\Delta/\Delta_{\text{Ref}}$ and $\tan \Psi/\tan \Psi_{\text{Ref}}$ are shown instead of the absolute ellipsometric parameters in order to extract the surface related signals from the overlapping bulk contribution. The ellipsometric parameters as determined directly after etching serve as the reference. In the top spectrum, which corresponds to the second spectrum after etching,

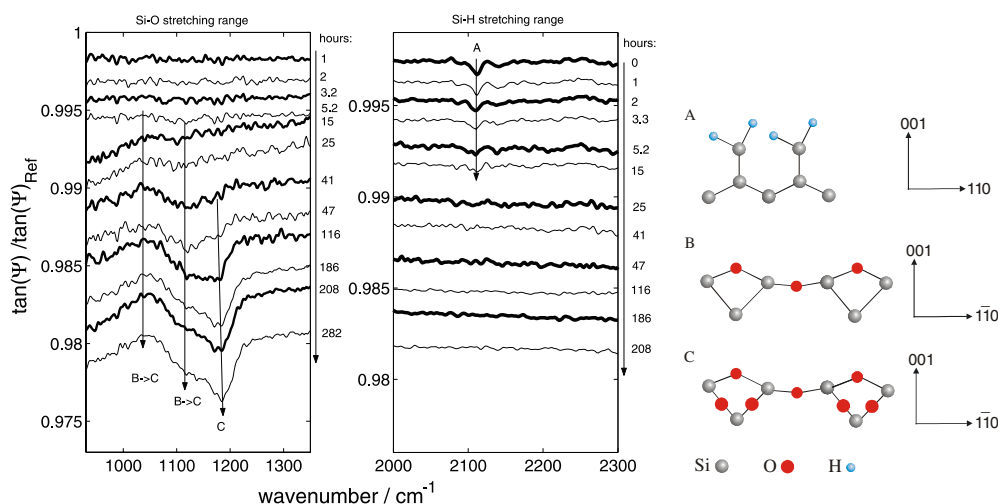


Figure 5. Left: $\tan \Psi / \tan \Psi_{\text{Ref}}$. Right: schematics for different adsorption geometries of H, Si-O-Si bridge bonds and oxidized back bonds ((A) is adapted from [44] and (C) is adapted from [1]).

(This figure is in colour only in the electronic version)

no surface related contribution is seen. Weak broad structures around 1050 and 1120 cm^{-1} already start to arise after 3.3 h . A third band only arises after 25 h at around 1177 cm^{-1} and is shifting towards higher wavenumbers upon exposure time in air. The weak bands around 1050 cm^{-1} (positive sign) and 1120 cm^{-1} (negative sign) appear before the hydrogen has been completely removed from the surface. Taking into account that no bands related to oxidized back-bonds have been observed in the Si-H spectral range this suggests that these bands are correlated with Si-O-Si or Si=O groups formed by replacement of the initial Si-H₂ groups at the surface. We assign these weak bands to the TO phonon and a Berreman-like band of the asymmetric Si-O-Si stretching vibration [42, 43].

The more prominent peak at about 1180 cm^{-1} is assigned to the oxidized back bonds. Its amplitude increases rapidly from the sixth (25 h) to the ninth (41 h) spectrum. In the latter spectra the change of band shape is much smaller. This observation could be explained by the kinetic of the back bond oxidation. According to the literature [17] the oxide interface is formed relatively quickly, while the subsequent oxide growth is diffusion limited and therefore much slower.

5. Summary

A stretching vibration of the SiH₂ group was identified at $2110\text{--}2113 \text{ cm}^{-1}$ and monitored in the initial steps of the oxidation. The reduction of amplitude of this band was found to originate from a gradually oxidizing surface, whereby most likely Si-O-Si bridge bonds are formed. This interpretation is supported by the occurrence of a band at 1050 cm^{-1} that is interpreted as the TO mode and a comparatively weak negative band at 1110 cm^{-1} interpreted as the related Berreman-like mode of the Si-O-Si bridge bond within only 3.3 h exposure time in air. In the later stages another contribution arises which is assigned to a Si-O-Si stretching vibration of the oxidized back bonds. Though this interpretation of the experimental findings is not unequivocal it agrees well with a number of models suggested for the SiO₂/Si(001) interface formation [1–6]. For an

overview the $\tan \Psi / \tan \Psi_{\text{Ref}}$ ratios are shown in figure 5, whereby the spectra in the Si–O stretching range are calculated taking the H-passivated surface as reference. In the Si–H stretching range the spectra are normalized to an oxidized surface.

Different proposed stages of oxidation are marked by (A)–(C) in figure 5: (A): hydrogen terminated surface, (B): Si–O–Si bridge bonds are formed at the surface replacing Si–H bonds, (C): oxidized back bonds. Since two different Berreman-like modes are observed it is concluded that the interface oxidizes in a step wise process. The structure of the interface is clearly different to fused quartz; the Berreman mode of a thin film is expected to occur at about 1235 cm^{-1} .

6. Conclusion

It has been shown that the initial steps of oxidation can be analysed by infrared ellipsometry in a single reflection geometry. Different surface geometries from the H-passivated surface to the oxidized interface are identified. The ellipsometric spectra show a direct correlation to the chemical bonds at the interface. A high potential is seen for further studies, e.g. exploring the orientation of the transition dipole moments of the Si–O–Si modes for selected stages of the interface formation by ellipsometric measurements at variable angles of incidence.

Acknowledgments

We acknowledge the technical support of Ilona Fischer from ISAS and of Regina Paßmann from the Technical University of Berlin. We also like to thank Dr Sandhya Chandola from Trinity College in Dublin for providing insights into the preparation of various silicon surfaces in ultra high vacuum.

The financial support by the Deutsche Forschungsgemeinschaft, the Senatsverwaltung für Wissenschaft, Forschung und Kultur des Landes Berlin and by the Bundesministerium für Bildung und Forschung is gratefully acknowledged.

References

- [1] Yamasaki T, Kaneta C, Uchiyama T, Uda T and Terakura K 2001 *Phys. Rev. B* **63** 115314
- [2] Bongiorno A and Pasquarello A 2003 *Appl. Phys. Lett.* **83** 1417
- [3] Uchiyama T, Uda T and Terakura K 2001 *Surf. Sci.* **474** 21
- [4] Schulte J, Ushio J and Maruizumi T 2000 *Thin Solid Films* **369** 285
- [5] Choi C H, Liu D-J, Evans J W and Gordon M S 2002 *J. Am. Chem. Soc.* **124** 8730
- [6] Kato K, Kajiyama H, Heike S, Hashizume T and Uda T 2001 *Phys. Rev. Lett.* **86** 2842
Kato K and Uda T 2000 *Phys. Rev. B* **62** 15978
- [7] Stallenberger J R 1996 *J. Vac. Sci. Technol. A* **14** 693
- [8] Fuyuki T, Muranaka S and Matsunami H 1997 *Appl. Surf. Sci.* **117/118** 123
- [9] Harada Y, Niwa M, Nagatomi T and Shimizu R 2000 *Japan. J. Appl. Phys.* **39** 560
- [10] Ikeda H, Nakagawa Y, Toshima M, Furuta S, Zaima S and Yasuda Y 1997 *Appl. Surf. Sci.* **117/118** 109
- [11] Herbots N, Shaw J M, Hurst Q B, Grams M P, Culbertson R J, Smith D J, Atluri V, Zimmerman P and Queenney K T 2001 *Mater. Sci. Eng. B* **87** 303
- [12] Namba K, Komeda T and Nishioka Y 1997 *Appl. Surf. Sci.* **117/118** 198
- [13] Clark K B, Bardwell J A and Baribeau J-M 1994 *J. Appl. Phys.* **76** 3114
- [14] Yasuda T, Yamasaki S, Nishizawa N, Miyata N, ShklyaeV A, Ichikawa M, Matsudo T and Ohta T 2001 *Phys. Rev. Lett.* **87** 037403
- [15] Saccani J, Buffeteau T, Desbat B and Blaudez D 2003 *Appl. Spectrosc.* **57** 1260
- [16] Vallant T, Brunner H, Kattner J, Mayer U, Hoffmann H, Leitner T, Friedbacher G, Schügerl G, Svagera R and Ebel M 2000 *J. Phys. Chem. B* **104** 5309
- [17] Miura T, Niwano M, Shoji D and Miyamoto N 1996 *Appl. Surf. Sci.* **100/101** 454

- [18] Cui Z and Takoudis C G 2001 *J. Appl. Phys.* **89** 5170
- [19] Queeney K T, Fukidome H, Chaban E E and Chabal Y J 2001 *J. Phys. Chem. B* **105** 3903
- [20] Sugita Y and Watanabe S 1998 *Japan. J. Appl. Phys.* **37** 3272
- [21] Rouchon D, Rochat N, Gustavo F, Chabli A, Renault O and Besson P 2002 *Surf. Interface Anal.* **34** 445
- [22] Tonova D, Depas M and Vanhellefont J 1996 *Thin Solid Films* **288** 64
- [23] Herzinger C M, Johs B, McGahan W A and Woollam J A 1998 *J. Appl. Phys.* **83** 3323
- [24] Ossikovski R, Drévilion B and Firon M 1995 *J. Opt. Soc. Am. A* **12** 1797
- [25] Brunet-Bruneau A, Rivory J, Rafin B, Robic J Y and Chaton P 1997 *J. Appl. Phys.* **82** 1330
- [26] Brunet-Bruneau A, Fisson S, Gallas B, Vuye G and Rivory J 2000 *Thin Solid Films* **377/378** 57
- [27] Boultaidakis S, Logothetidis S, Papadopoulos A, Vouroutzis N, Zorba Ph, Girginoudi D and Thanailakis A 1995 *J. Appl. Phys.* **78** 4164
- [28] Brunet-Bruneau A, Fisson S, Vuye G and Rivory J 2000 *J. Appl. Phys.* **87** 7303
- [29] Ono H, Ikarahi T, Ando K and Kitano T 1998 *J. Appl. Phys.* **84** 6064
- [30] Fenner D B, Biegelsen D K and Bringans R D 1989 *J. Appl. Phys.* **66** 419
- [31] Röseler A 1993 *Thin Solid Films* **234** 307
- [32] Röseler A 1990 *Infrared Spectroscopic Ellipsometry* (Berlin: Akademie Verlag)
- [33] Azzam R M A and Bashara N M 1977 *Ellipsometry and Polarized Light* (Amsterdam: North-Holland)
- [34] Hinrichs K, Tsankov D, Korte E H, Röseler A, Sahre K and Eichhorn K-J 2002 *Appl. Spectrosc.* **56** 737
- [35] De Gryse O and Clauws P 2000 *J. Appl. Phys.* **87** 3294
- [36] Watanabe S 1998 *J. Chem. Phys.* **108** 5965
- [37] Angermann H, Henrion W, Rebien M, Fischer D, Zettler J-T and Röseler A 1998 *Thin Solid Films* **313/314** 552
- [38] Mazzara C, Jupille J, Zheng W-Q, Tanguy M, Tsadjeddine A and Dumas P 1999 *Surf. Sci.* **427/428** 208
- [39] Tagami K, Tsuchida E and Tsukada M 2000 *Surf. Sci.* **446** L108
- [40] Uemura S, Fujii M, Hashimoto H and Nagai N 2001 *Japan. J. Appl. Phys.* **40** 5312
- [41] Röseler A and Korte E H 2001 *Handbook of Vibrational Spectroscopy* vol 2, ed P R Griffiths and J Chalmers (Chichester: Wiley)
- [42] Kandilioti G, Siokou A, Papaefthimiou V, Kennou S and Gregoriou V G 2003 *Appl. Spectrosc.* **57** 628
- [43] Wang J, Zou B and El-Sayed M A 1999 *J. Mol. Struct.* **508** 87
- [44] Freking U, Krüger P, Mazur A and Pollmann J 2004 *Phys. Rev. B* **69** 035315
- [45] Berreman D W 1963 *Phys. Rev.* **130** 2193
- [46] Yamada-Kaneta H, Kaneta C and Ogawa T 1990 *Phys. Rev. B* **42** 9650