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Second-Harmonic Generation: A New Technique for Probing Chemical Bonding on Vicinal Si(III) Surfaces

C.H. Bjorkman*, T. Yasuda*, G. Lucovsky*, U. Emmerichs**, C. Meyer**, K. Leo**, and H. Kurz**
*Departments of Physics, Materials Science & Engineering, and Electrical & Computer Engineering,
North Carolina State University, Raleigh, North Carolina 27695-8202, U.S.A.
**Institute of Semiconductor Electronics II,
Rheinisch-Westfälische Technische Hochschule, 5100 Aachen, Germany

Using Second-Harmonic Generation (SHG) pumped at 1053 nm, the influence of off-axis orientation and surface structure of Si (111) surfaces was examined. The surface structure was modified by oxidation, annealing, and removing the oxide in an HF solution. Different rotational anisotropies of the detected SHG signal were observed for H-terminated and O-terminated surfaces. In addition, the rotational anisotropy changed after annealing at temperatures in the range of 900°C - 1100°C. These changes in the characteristic rotational anisotropies were analyzed using harmonic functions reflecting the onefold and threefold symmetry of vicinal Si(111) surfaces, and compared with changes in the interface state density upon annealing.

1. INTRODUCTION

Second-harmonic generation (SHG) is a sensitive probe for surface studies of centrosymmetric media [1-3]. Recent investigations on Si-SiO_2 heterostructures showed that SHG can be used to study this technologically important materials system [4-7].

The generated electric field at the second harmonic frequency $E(2\omega)$ is due to a nonlinear polarization $P(2\omega)$ that is determined by the susceptibility tensor $X^{(2)}$:

$$E_l(2\omega) \propto P_l(2\omega) \approx \chi^{(2)}_{lmn} E_m(\omega)E_n(\omega). \qquad (1)$$

For silicon, a centrosymmetric crystal, $X^{(2)}$ is only non-zero in the electric dipole approximation at the surface where the bulk symmetry is broken. However, additional higher order processes from the bulk can also contribute to the SHG signal. For the case of a modified, e.g. oxidized, surface the change in SHG response gives information about the changes in the chemical bonding or local atomic arrangements at the surface. It has been reported [5], that for oxidized silicon surfaces the second harmonic signal originates from the first few oxide layers and strain effects in the underlying silicon influence the signal less than 10%. For off-axis oriented Si(111) surfaces, a change in rotational anisotropy of the signal is observed when the sample is rotated about the surface normal. This behavior has been attributed to the tilt of the crystal [6] or to contributions from atomic steps at the surface [7].

In this paper, we report on the SHG response of vicinal Si(111) surfaces, stepped in [11$\bar{2}$] direction for different offset angles. SHG has been shown to be a sensitive probe for studying steps on vicinal Si(111) substrates, and can also be used to differentiate between O- or H-atom termination of dangling bonds on such surfaces [8-9]. We find that these chemical modifications of the interface result in dramatic changes of the nonlinear optical response. We also investigate the effects of rapid thermal annealing and also correlations between the electrical properties of, and second-harmonic generation at, Si-SiO_2 interfaces.

2. EXPERIMENTAL PROCEDURES

The SHG experiments were performed on Si(11$\bar{1}$) samples with a tilt angle between 0° and 5° in the [11$\bar{2}$] direction. About 60 nm of thermal oxide was grown at 850°C in a dry oxygen ambient. Rapid Thermal Annealing (RTA) was performed on some of these samples at temperatures ranging from 900°C to 1100°C in a dry argon atmosphere, containing sufficient O_2 to prevent reduction of the oxide layer on the Si surface. At this stage, Al dots were formed on some samples to investigate correlations between SHG and electrically active defects at the Si-SiO_2 interfaces. The electrical characterization was performed using the combined high-frequency and quasi-static C-V method. Finally, all oxide was removed and the freshly etched, H-terminated surface was investigated.

A Nd:YLF regenerative amplifier operating at 1 kHz and seeded by a cw-mode locked Nd:YLF oscillator produced the 1053 nm pump light used in the SHG experiments. The 40 ps laser pulses were filtered by a glass filter and a polarizer before striking the rotating sample at an incident angle of 45 degrees with a spot size of ~2 mm and energy per laser pulse of about 0.5 mJ. The reflected fundamental laser light and the third harmonic were suppressed by a combination of dichroic

mirrors, glass filters and a polarizer, while the generated second-harmonic signal was focused into a single photon counting photomultiplier. All results presented in this paper were obtained using s-polarized pump light and by detecting the s-polarized SHG signal. To suppress any background signal, the counting electronics were "gated" by the laser with a gate width of ~1 ms. A schematic of the experimental setup and the sample geometry can be found in Reference 9.

3. EXPERIMENTAL RESULTS

We first discuss the results of SHG studies of vicinal Si(111) wafers. By using vicinal wafers with steps in the [11$\bar{2}$] direction, a mirror plane azimuthal symmetry component, C_{1v}, is mixed with the intrinsic threefold symmetry, C_{3v}, of the SHG response from a Si(111) surface. There are two experimental observations for the oxidized Si(111) surfaces i) the fraction of the C_{1v} symmetry signal increases as the vicinal angle increases, and ii) for surfaces oxidized below 850°C, the relative phase of the C_{1v} and C_{3v} signals changes abruptly when these surfaces are annealed at temperatures of 900°C and higher (see Fig. 1). The first of these observations establishes that the C_{1v} component derives from local atomic bonding arrangements at the surface steps, and the second establishes that there are atomic rearrangements of the Si and O-atoms at the surface steps for processing temperatures of 900°C and above. We have also noted that for interface formation and/or annealing done at temperatures below 900°C, the azimuthal dependence of the SHG signals, i.e., the mixing of the C_{1v} and C_{3v} signals, are all essentially the same. These processes have included thermal oxidation at 850°C, plasma-assisted oxidation and deposition at 300°C, and chemical oxidation at room temperature [10].

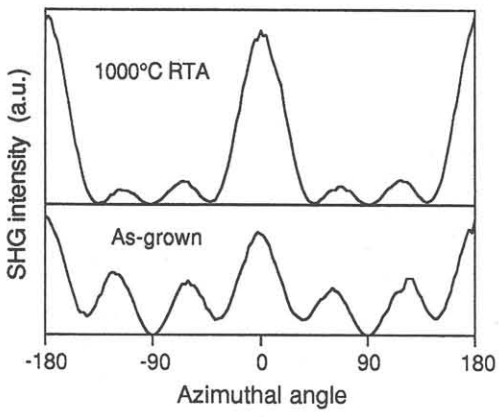

Fig. 1. SHG intensity (ss-geometry) as a function of angle of rotation from SiO_2/Si interfaces. These interfaces were formed by thermal oxidation at 850°C, and by additional anneal at 1000°C on 5° vicinal wafers.

Figure 2 shows the difference in rotational anisotropy between an interface formed by thermal oxidation at 850°C and an H-terminated surface obtained after removing the oxide in buffered HF. As will be discussed below, the mixing of C_{1v} and C_{3v} can again explain the observed difference.

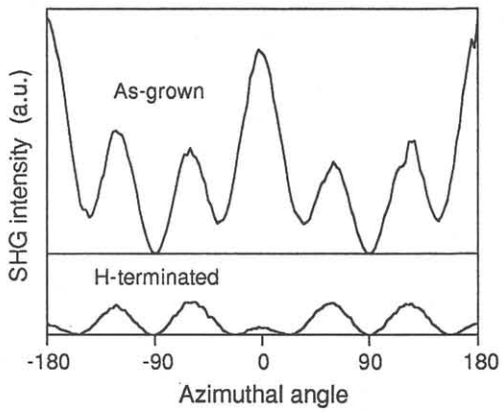

Fig. 2. SHG intensity as a function of angle of rotation from O- and H-terminated 5° vicinal Si(111) surfaces.

For Si/SiO_2 interfaces formed by thermal oxidation at 850°C, the electrical properties improve when subjected to a higher temperature rapid thermal anneal, e.g., at 900 to 1050°C. There is small reduction in the interface state density, D_{it}, at midgap after annealing at 900°C, and a more significant decrease when the annealing temperature is increased to 1000°C, as is shown in figure 3.

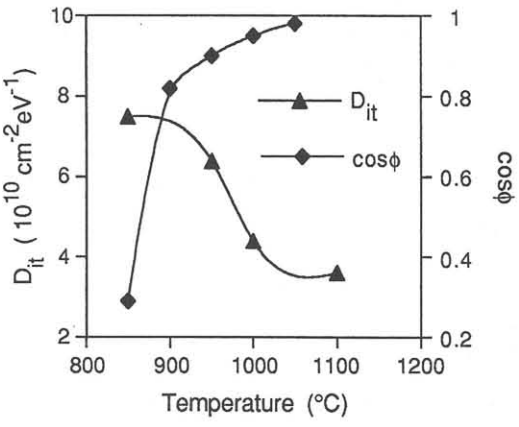

Fig. 3. Midgap D_{it} and $\cos\phi$ vs. growth or annealing temperature. ϕ is the phase angle between the C_{3v} and C_{1v} contributions.

4. DISCUSSION

The combination of the SHG and electrical properties studies on the Si(111) structures fabricated by thermal oxidation has allowed us to separate two different effects that contribute to interfacial electrical quality. For the thermally-grown oxides, prepared at 850°C, there is considerable compressive intrinsic

growth strain in the bulk oxide film [11,12]. The relaxation of this strain requires temperatures of approximately 1000°C. In a previously published study, it was shown that the defect density at the SiO_2/Si interface was proportional to the intrinsic oxide strain, and that annealing to temperatures in excess of 1000°C reduced both the strain and midgap D_{it} [13]. We show in Fig. 3, that there is a small reduction in D_{it} at 900°C, correlated with the interfacial bonding rearrangements as monitored by the SHG results, and then a significantly larger decrease at 1000°C after visco-elastic relaxation of the bulk oxide strain.

The SHG results from vicinal Si(111) surfaces suggest that the onefold contribution to the SHG signal originates primarily from the Si atoms at, or in the immediate vicinity of the surface steps, and that these signals are associated with Si-O and Si-H bonds that have in-plane projections in the $[11\bar{2}]$ direction. Moreover, a Fourier analysis of the data showed that the onefold and threefold symmetry components dominate, i.e. we found negligible isotropic and twofold components. A general expression for the generated second-harmonic field $E(2\omega)$ is given in Eqn. (2):

$$E(2\omega) = A_1\cos(\Psi) + A_3\cos(3\Psi)e^{i\phi}\,. \qquad (2)$$

Fitting this expression to the measured intensities yield information about the amplitudes of the onefold and threefold contributions, A_1 and A_3, respectively, and the relative phase between the two contributions, ϕ. An alternative expression for $E(2\omega)$ is shown in Eqn.(3):

$$E(2\omega) = A_1\cos(\Psi) + (a_3 + ib_3)\cos(3\Psi)\,, \qquad (3)$$

where $a_3 = A_3\cos\phi$ and $b_3 = A_3\sin\phi$. If the threefold component was purely imaginary (relative to the onefold component), then there would be no interference, constructive or destructive, between the two contributions. Therefore, $\cos\phi$ is then a measure of the interference between the onefold and threefold components. Deposited and as-grown thermal oxides exhibit similar levels of interference [10], while the anneal at 950°C increases the interference significantly. After an anneal at 1000°C the interference is near total, $\cos\phi$ = 0.95. This temperature range is the same at which SiO_2 flows and also significant reductions in interface state density took place when C-V measurements were performed on the same set of samples. It is therefore likely that changes in chemical bonding arrangements at steps on vicinal Si(111) surfaces influences both the nonlinear optical response as well as the density of electrically active defects.

Applying the same analysis to SHG response from H-terminated surfaces yielded a surprising destructive interference between the onefold and threefold components of SHG signal. At this stage, we offer no explanation for the change from constructive interference in the case of annealed Si-SiO_2 structures to destructive interference after removing the oxide.

We have also compared the midgap D_{it} and SHG data for the Si-SiO_2 structures prepared by thermal oxidation, and then subjected to rapid thermal annealing. Figure 3 displays a comparison of these data plotted as function of the highest processing temperature employed, either the thermal oxidation temperature of 850°C, or the rapid thermal annealing temperature. We note a modest decrease in D_{it} between processing temperatures of 850°C and 950°C, a more rapid decrease between 950°C and 1000°C, finally followed again by a slower decrease between 1000°C and 1100°C. The behavior of the SHG ratio is qualitatively different. $\cos\phi$ increases dramatically between 850°C and 900°C, and then increases more gradually as the temperature is further increased.

5. CONCLUSIONS

We have observed large changes in the interference between the onefold and threefold contributions to the SHG signal from vicinal Si(111) surfaces. These changes are associated with changes in the chemical bonding at the surface steps. This is clearly evident from the combination of data from the thermally-oxidized and annealed interfaces, and from the H-terminated Si surfaces. These changes in bonding may also be responsible for the relatively small decrease in D_{it} between 850°C and 900°C for the thermally-oxidized and annealed Si-SiO_2 interfaces. The slower rate of increase of the SHG ratio for temperatures higher than 900°C may be associated with stress relaxation in the bulk of the oxide film.

REFERENCES

1) N. Bloembergen, R. K. Chang, S.S. Jha, and C.H. Lee, Phys. Rev. **174** (1968) 813.
2) C. C. Wang, W.W. Duminski, Phys. Rev. Lett. **20**(1968) 668; C.C. Wang, Phys. Rev. **178**(1969) 1457.
3) H.W.K. Tom, T.F. Heinz, Y.R.Shen, Phys. Rev. Lett. **51**(1983) 1983.
4) C.W. van Hasselt, M.A: Verheijen, Th. Rasing, Phys. Rev. B **42**(1990) 9263.
5) L.L. Kulyuk, D.A. Shutov, E.E. Strumban, O.A. Aktsipetrov, J. Opt. Soc. Am. B **8**(1991) 1766.
6) R.W.J. Hollering and M. Barmentlo, Optics Communications. **88**(1992) 141.
7) M.A: Verheijen, C.W. van Hasselt, Th. Rasing, Surface Science **251/252**(1991) 467.
8) C.H. Bjorkman, C.E. Shearon, Jr., Y. Ma, T. Yasuda, G. Lucovsky, U. Emmerichs, C. Meyer, K. Leo and H. Kurz, to be published in J. Vac. Sci. Technol. **A11**(1993).
9) U. Emmerichs, C. Meyer, K. Leo, H. Kurz, C.H. Bjorkman, C.E. Shearon Jr., Y. Ma, T. Yasuda, and G. Lucovsky, to be published in MRS Symp. Proc. **281**.
10) C.H. Bjorkman, T. Yasuda, C.E. Shearon Jr., Y. Ma, G. Lucovsky, U. Emmerichs, C. Meyer, K. Leo, and H. Kurz, to be published in J. Vac. Sci. Technol. **B11** (1993).
11) E.A. Irene, E. Tierney, and J. Angilello, J. Electrochem. Soc. **129**(1982) 2594.
12) J.T. Fitch, E. Kobeda, G. Lucovsky, and E.A. Irene, J. Vac. Sci. Technol. **B7**(1989) 153.
13) C.H. Bjorkman, J.T. Fitch and G. Lucovsky, Appl. Phys. Lett. **56**(1990) 1983.