INVESTIGATION OF THE Si(111)-(7 × 7) SURFACE BY SECOND-HARMONIC GENERATION: OXIDATION AND THE EFFECTS OF SURFACE PHOSPHORUS

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We have studied the initial stages of oxidation, the temperature dependence of the surface electronic structure, and the effect of phosphorus on oxidation of the Si(111)-(7×7) surface using optical second-harmonic generation. We have also observed a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern due to surface reconstruction induced by < 0.5% P on Si(111).

1. Introduction

The importance of controlling and characterizing the $Si–SiO_2$ and Si–metal interfaces has focused attention on the atomic-scale chemistry and physics of those interfaces. Recently, we demonstrated that optical second-harmonic generation (SHG) being capable of selectively responding to surface electronic properties, could be an effective in situ probe of atomic and molecular adsorption on a metallic surface [1]. Here, we show that SHG is equally sensitive to the surface electronic properties of the Si surface. We have used SHG to study the kinetics of the growth and thermal desorption of the first two surface oxide layers, temperature-dependent changes on the surface electronic properties which are coincident with the segregation of < 0.5% monolayer of phosphorus, and the effect of surface P on the growth of the first oxide layer. While the importance of P segregation has been studied for highly-doped ($10^{20}/cm^3$) samples [2], it has not been full appreciated in relatively pure samples with low phosphorus concentration ($10^{15}/cm^3$). We report here for the first time that P segregation on the Si(111) surface appears to have the effect of being able to induce a surface reconstruction evidenced by a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern.

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2. Experiment

Experiments were performed in an ultrahigh vacuum chamber typically operated at 7×10^{-10} Torr and equipped with low energy electron diffraction (LEED) and a retarding field analyzer for Auger electron spectroscopy (AES). The Si(111) wafers (0.010 inch thick, $10^{15} cm^3$ P-doped) were supported by Ta clips which also served as electrodes for direct ohmic heating. Sample temperatures ($\pm 50°C$) were monitored with an optical pyrometer. For SHG measurements, frequency-doubled Nd^{3+}:YAG laser pulses at 532 nm with 7 ns duration and ~ 10 mJ energy were incident on the sample at 45° with a 6 mm beam diameter. The reflected SH signal was detected with a photomultiplier and processed with gated electronics.

Si surfaces were cleaned by thermal annealing at 1100°C in $\sim 10^{-9}$ Torr vacuum for < 2 min. This treatment left negligible oxygen and only a small amount of carbon on Si (the ratios of AES peaks obtained with 2 keV beam energy were $O_{507}/Si_{92} < 5 \times 10^{-4}$ and $C_{270}/Si_{92} = 1.5 \times 10^{-2}$). Final cleanliness was monitored with the SH intensity which, as described below, was extremely sensitive to surface oxygen. We found this essential as the 60 μA electron current from the Auger gun induced considerable adsorption of oxygen even in $< 1 \times 10^{-9}$ Torr O_2. The appearance of the sharp (7×7) LEED pattern upon cooling the sample was taken as a further sign of nominal cleanliness. Laser irradiation during SHG measurements did not prevent the formation of the (7×7) pattern upon cooling, did not damage the optically polished sample surface for sample temperatures below 1100°C, and did not anneal the (7×7) pattern at room temperature to the laser-induced (1×1) surface structure [3]. However, several oxidation cycles followed by high temperature annealing caused surface roughening. Results reported here were therefore performed on samples with minimal cycling. We did not study systematically the role of laser irradiation in this roughening process.

3. Results and discussion

3.1. Oxygen adsorption kinetics on Si(111)

In fig. 1, we show the SH signal from the Si(111) surface held at two different temperatures during exposure to 10^{-6} Torr of O_2. At both temperatures, oxygen decreases the SH to a saturation level within the first 100 L of exposure. For the room temperature case (see curve 1a), the clean surface started with the (7×7) reconstruction and the SH signal fell to a saturation level 50% of its clean surface level at ~ 70 L due to the saturation of a chemisorbed oxide layer [4–6]. The O_{507}/Si_{92} Auger peak ratio after 120 L of O_2 exposure at room temperature was 1.0%, a figure we used to calibrate a full
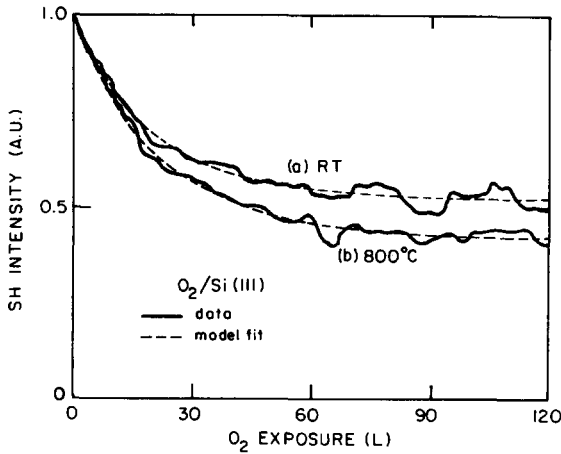
Fig. 1. SH intensity from the Si(111) surface at (a) RT and (b) 800°C during O_2 exposure (1 langmuir = 10^{-6} Torr s). The SH for the clean surface is normalized to 1.0. The dashed curves were fit to the data using a model described in the text.

chemisorbed monolayer of oxygen coverage. The SH data are not sensitive enough to distinguish between the presence of two possible adsorbed species: one (perhaps peroxy-radical) which is believed to be present at low coverage below 10 L exposure but absent at 100 L and one (perhaps bridge-bonded oxygen) which is present at all exposures through 100 L [5]. In fact, the SH intensity versus exposure curve fits quite well a simple model in which adsorption presumably occurring at only one type of site (namely, bridge-bonded O species), follows first-order Langmuir kinetics and the change in nonlinear response of the surface is directly proportional to coverage. The first assumption in the limit of negligible desorption allows the adsorbate coverage $\theta(x)$ in units of fractional monolayer to be given by:

$$\theta(x) = 1 - e^{-kx}, \tag{1}$$

where x is the exposure in langmuir and k is a proportionality constant dependent on the sticking coefficient. The second assumption allows the SH field magnitude, $E_{2\omega}(x)$, to be given by

$$E_{2\omega}(x) = A + B\theta(x), \tag{2}$$

where A and B are coefficients associated with the clean and adsorbate-induced surface nonlinearity. The dashed curve (a) in fig. 1 is obtained with $B/A = -0.278 \pm 0.003$ and $k = 0.045 \pm 0.002$ L^{-1}.

For oxidation at 800°C [see curve (b) of fig. 1], the SH was reduced by ~ 50% after ~ 30 L exposure at which point AES indicated that there was ~ 1.3 of an O-atom layer equivalent on the surface. The SH continues to drop

from 30 L through 70 L and changes very little after 70 L. These results are consistent with EELS [5] results suggesting that at ~ 70 L exposure the surface is saturated with a single adsorbed species and after ~ 70 L deeper layers of an oxide species with vibrational spectra resembling stoichiometric SiO_2 are formed. By 120 L, the AES O_{507}/Si_{92} ratio indicated the O coverage was equivalent to 2 monolayers. Because there is only one adsorbed species for the first 1 or 2 equivalent layers of oxygen, it is reasonable that the 800°C data from 0 to 70 L should again be fit with the single-site Langmuir model usings eqs. (1) and (2). The dashed curve (b) in fig. 1 was obtained with $B/A = -0.343 \pm 0.003$ and $k = 0.04 \pm 0.002$ L^{-1}. No change in the SH could be detected for further O_2 exposure over 2 monolayers. The lack of SH sensitivity to the growth of additional layers after the first 2 is consistent with SH being intrinsically sensitive only to the symmetry-broken surface layer of a centro-symmetric medium.

The success of the Langmuir model suggests that SHG is not sensitive to the different oxide species known to form on Si [5,7,8]. One might think that the SH susceptibility of Si(111) would be dominated by the surface dangling bonds and quenching of the dangling bonds by adsorbed oxygen would lead to a decrease in SHG. However, photoemission work on Si indicates that most of the dangling bonds are quenched with only 10 L oxygen exposure [9]. SHG must therefore be dominated by transitions between other surface states which are reduced by adsorption of any oxygen species. It should be most sensitive to transitions in the visible because of near-resonance enhancement. EELS studies on RT Si(111)-(7 × 7) surface show strong loss peaks at 1.7, 3.5, and ~ 5 eV due to transitions between surface states other than dangling bonds [4,10]. The 1.7 and 3.5 eV EELS peaks [11] are observed to decrease continuously through the adsorption of the first layer of oxygen as did the SH intensity. This suggests that the SH signal is probably dominated by the same surface electronic transitions that appear in EELS. As for the part of the SH that remains after the thermal growth of a multilayer oxide, it may be due to the transitions giving rise to the 5 eV EELS peak (which does not decrease with oxygen exposure [3]) and to the dipole-forbidden SH susceptibility of the Si bulk [12].

3.2. Kinetics of thermal desorption of oxygen from Si(111)

We also used SHG to probe the thermal desorption kinetics of oxygen from Si(111). The sample heated to 900°C was exposed to ~ 40 L of O_2 at 10^{-6} Torr. The O_2 leak valve was then closed and the sample temperature kept unchanged. Within ~ 2 min of closing the leak valve, the chamber background pressure was $< 3 \times 10^{-9}$ Torr. The SH signal, as shown in fig. 2, returned to the ~ 50% level in ~ 2 min, whereupon AES showed that there was ~ 1 monolayer equivalent of oxygen remaining. The rate of this signal restoration
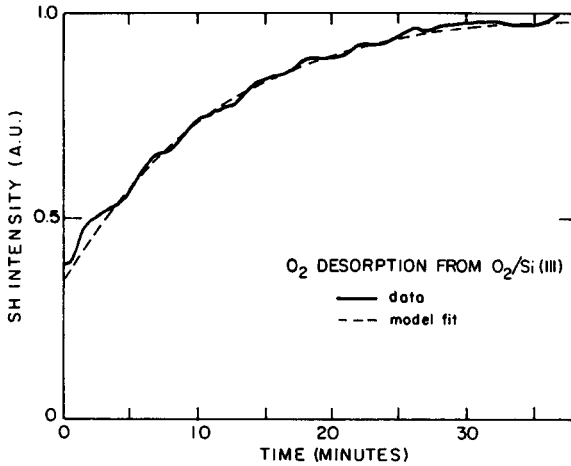
Fig. 2. SH intensity from the Si(111) surface held at 900°C as a thermally grown oxide layer desorbs from the surface. The time axis begins immediately after the surface is exposed to 40 L of O_2.

could not be measured accurately as the background pressure could not be controlled well enough to make the adsorption rate negligible during this short initial stage. Desorption of the remaining oxygen after the initial 2 min, however, was no longer affected by adsorption. It is reasonable to believe that the remaining oxygen was bound to the top surface layer. SHG responding to the desorption of this layer of oxygen can again be modelled by Langmuir kinetics and by assuming the SH depends on oxygen coverage as in eq. (2). In this case, however, oxygen desorbs from a single site with a rate depending only on the oxygen surface coverage so that the time-dependence of oxygen coverage is $\theta(t) = \exp(-kt)$. The data of fig. 2 are fit with $B/A = -0.412$ and $k = 1.7 \times 10^{-3}$/s. The same measurement performed at a sample temperature of 1100°C yielded $k = 5.3 \times 10^{-2}$/s. If we assume there is only a single activation energy such that $k = \nu_0 \exp(-E_d/k_BT)$, where ν_0 is a pre-exponential factor, E_d is the energy of desorption and k_B is the Boltzmann constant, then E_d is 2.3 eV and $\nu_0 = 4.0 \times 10^7$/s. This activation energy may be compared to the 3.5 eV energy reported in ref. [13] for temperatures between 700 and 750°C. Disagreement may imply that there is more than one desorption mechanism. However, it is more likely due to the difference in the initial surface oxide coverages; in ref. [13], the Si surface was initially covered by multi-layers of oxide.

3.3. Temperature dependence of SHG from Si(111)

The SH signal from a bare Si(111) surface appeared to depend on temperature. When the native oxide layer was removed by thermal desorption from a
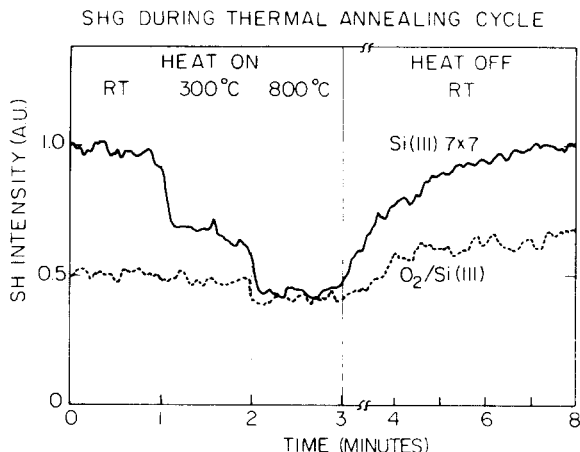
SHG DURING THERMAL ANNEALING CYCLE

Fig. 3. SH intensity from the nominally clean 7×7 reconstructed (————) and RT-oxidized
(— — —) Si(111) surface during a thermal cycle in which the sample is held at 300 and 800°C for
one minute each and then allowed to cool.

new sample, we found that the SH increased as the nominally clean sample
cooled from 1100°C to room temperature. After two more annealing cycles
with the sample heated to 1100°C for 2 min, the temperature dependence of
SH during annealing cycles was reproducible and reversible, as shown by the
solid curve of fig. 3. The SH at room temperature was about twice that at
800°C. This effect must arise from temperature-dependent changes in the
surface electronic properties of Si(111). Recent EELS measurements [10] show
that sharp loss peaks associated with transitions to an unoccupied dangling
bond state just above the Fermi level, broaden and disappear as the Si(111)-(7
× 7) surface is warmed from 70 K to RT. This change is attributed to thermal
occupation of the final state leading to a reduction of the transition probabili-
ties. Of particular interest here, the EELS loss peak at 1.7 eV is reduced by a
factor of ∼ 2 from 70 K to RT. Other EELS studies [14] show that the 1.7 eV
peak disappeared as the sample is heated from RT to 865°C and the order of
the surface changes from (7 × 7) to (1 × 1). The observed change of SHG with
temperature may well be due to the temperature dependence of the 1.7 eV
transition.

3.4. Effects of phosphorus segregation on Si(111)

Part of the observed temperature-dependent change of SHG may also be
due to segregation of phosphorus from the Si bulk to the surface at lower
temperature. In fig. 4 we show the 120 eV AES peak [15] of P on the nominally
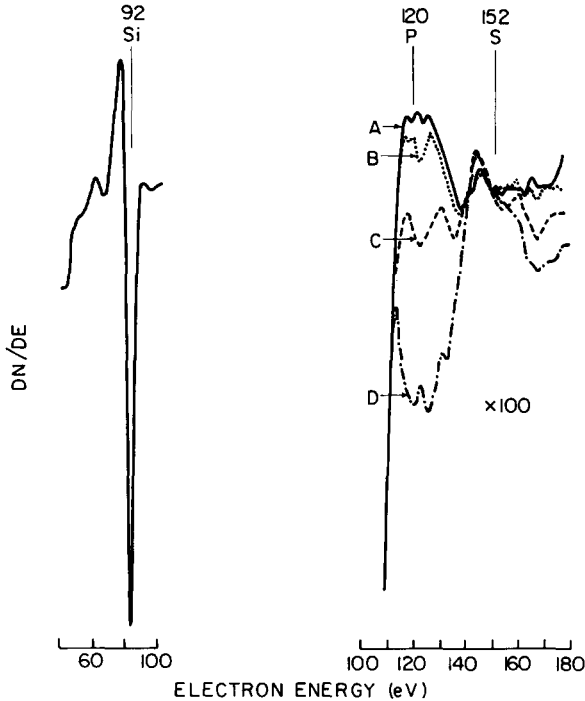clean Si surface at several temperatures. The small (negative-going) peak at RT

Fig. 4. Auger electron spectrum of P segregated on the Si surface at different temperatures: (A) 1000°C, (B) 500°C, (C) RT after quick cooling, (D) RT after cooling at 100°C/min.

decreases and broadens as the temperature is raised. The large width and the splitting of the P peak into two may be due to P being in different local environments, e.g., coordinated with different numbers of Si or in structural defects [16]. The data show that the SH increase and decrease correlate with the RT segregation of P to the surface and the diffusion of P from the surface back into the bulk at elevated temperatures. Typically, when we cooled the sample from 1100°C to RT quickly [17], the P_{120}/Si_{92} ratio was ~ 0.001 to 0.002. However, the larger P_{120}/Si_{92} ratio of 0.005 shown in fig. 4 was obtained by cooling the sample from 1100°C at ~ 100°C/min. Assuming the Auger sensitivities for Si and P are the same, we may estimate the P concentration on the surface to be ~ 0.5% of a Si monolayer or 4×10^{12} atoms/cm². Such a concentration is surprisingly large when one considers that the entire sample should only contain 3×10^{13} P atoms/cm². The mechanism for this segregation is unknown; however, the segregation of P at the Si/SiO_2 interface to a stable surface trap is a well-studied problem for heavily-doped (1 > 10^{19}/cm³) samples [2,16]. In those studies [2], it was found that the accumulation of P at the surface was accompanied by a depletion of P in a region ~ 50 Å below the surface. Since AES only detects atoms in the top ~ 20 Å, the AES

results could be due to P diffusing to the depletion zone at high temperatures and resegregating to the surface at lower temperatures. At this time, we can only comment that the ability of P to relieve surface strain and to bend the surface electronic bands make plausible an extremely deep yet temperature-dependent surface trap for P. P-induced changes to the surface electronic properties may cause some of the observed increase in the SH signal; however, increasing the P concentration from 0.1 to 0.5% of a monolayer did not substantially increase the SH. The large amount of P could be reduced to the 0.0008 level by reheating the sample and then cooling quickly.

The segregation of P to the surface did appear to affect SHG from the oxidized Si surface. After the RT surface was oxidized the SH signal was not reversible in heating cycles up to 800°C (see the dashed curve of fig. 3) even though AES indicated that the surface O and P concentrations were un-changed. This indicates that the annealing cycle induces the formation of new SiP or SiP_xO_y complexes on the oxidized surface. When the sample was predosed with a RT chemisorbed-oxygen layer and then immediately heated to 1100°C, the SH increased (consistent with the desorption of oxygen) and then fell (due to the diffusion of P) to the SH level corresponding to a clean Si sample heated to 1100°C. This suggests that the surface oxygen stabilized the segregated P on the surface and that O had to be removed from the surface before P could diffuse back into the bulk. The importance of P segregation for Si with low levels of P-doping is noteworthy since much of the work on oxidation of the "clean" (7 × 7) surface of Si(111) has been performed on such samples.

The strong interaction of P with the surface structure of Si is underscored by the observation of a new LEED pattern associated with the segregation of P to the surface. After several thermal cycles using slow cooling rates, the (7 × 7) pattern became more difficult to see and as the RT P_{120}/Si_{92} peak ratio was increased to ~ 0.5%, a sharp ($\sqrt{3} \times \sqrt{3}$)R30° pattern gradually appeared. This is the first observation of such a LEED pattern. Because there was so little P on the surface, the sharp ($\sqrt{3} \times \sqrt{3}$)R30° pattern is probably not due to a P overlayer, but rather to a P-induced reconstruction. Comparable (~ 1%) amounts of Te [18] and Cl [19] have been observed to induce (1 × 1) recon-structions on the Si(111)-(7 × 7) surface; however, the ability of P to coordi-nate with Si as a donor, to effect oxygen chemistry and to induce a different ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern makes this case different enough to suggest a different reconstruction mechanism deserving further investigation.

4. Conclusion

We have studied the growth and thermal desorption kinetics of surface oxide on Si(111) using a purely optical technique, SHG. In both cases, the

results are found to fit well with the Langmuir kinetics assuming only one type of adsorption site is involved. It suggests that SHG must be dominated by surface electronic transitions which do not have the sensitivity to distinguish the different oxide species possibly formed on Si. The temperature dependence of SHG from bare Si indicates that the surface electronic properties do vary appreciably with temperature. We have also used SHG to monitor the effect of minute amounts of surface phosphor on the oxidation of Si(111). These results clear the way for further SHG studies of semiconductor interfaces and suggest that SHG diagnostics might be useful in the fabrication of well-characterized semiconductor devices. In the course of our SHG investigations, we have found that surface segregation of phosphorus (and perhaps other donors as well) even in lightly doped ($10^{15}/cm^3$) Si can induce a ($\sqrt{3} \times \sqrt{3}$) R30° surface reconstruction of Si(111).

Acknowledgements

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