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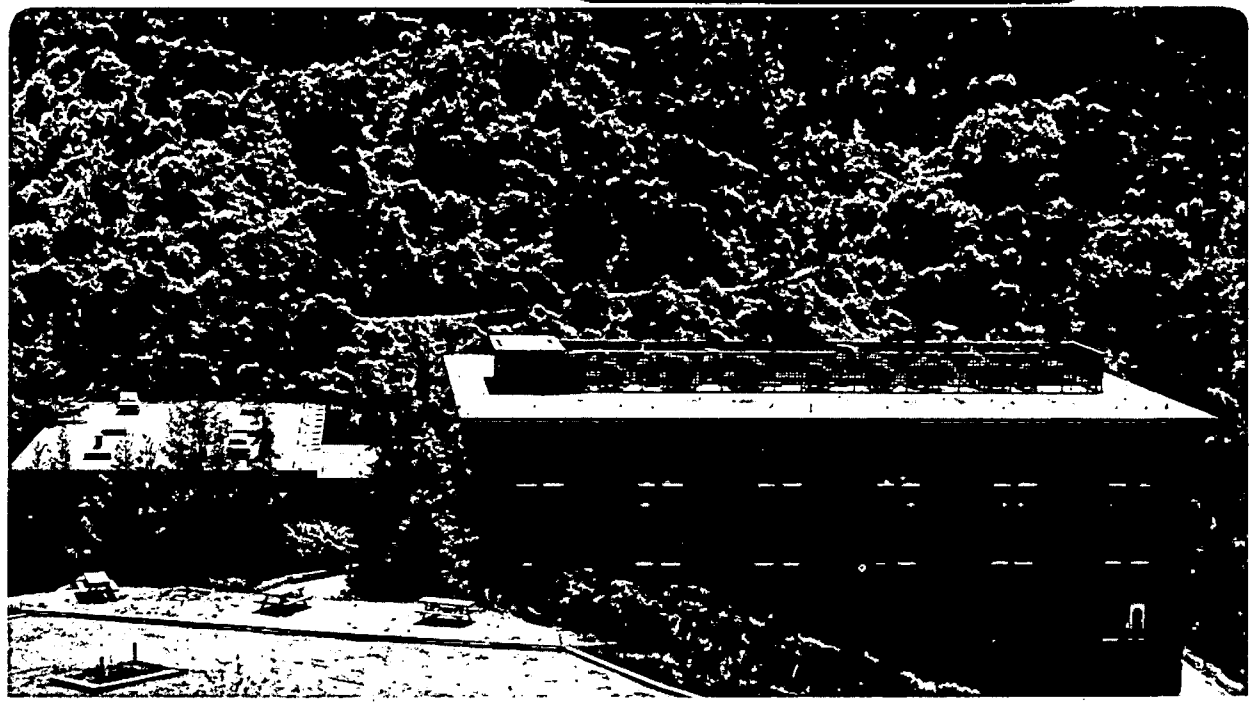## Materials & Molecular Research Division

INVESTIGATION OF THE Si(111) SURFACE IN UHV:
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INVESTIGATION OF THE Si(111) SURFACE IN UHV:

OXIDATION AND THE EFFECT OF SURFACE PHOSPHORUS

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We have studied the initial stages of oxidation, the segregation
of phosphorus, and the effect of phosphorus on oxidation of the
Si(111) 7 X 7 surface using optical second-harmonic generation. We
have also observed a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern for P on Si(111).

The importance of controlling and characterizing the electronic properties of Si-
SiO_2 and Si-metal interfaces has prompted great interest in the atomic-scale chemistry and
physics of those interfaces. Here, we report an investigation of the clean Si(111) 7 X 7
surface under low pressure oxidation and thermal annealing. Recently[1], we demonstrated
that optical second-harmonic generation (SHG) could be an effective in situ probe of atom-
ic and molecular adsorption on a metallic surface. Here, we show that SHG is equally sen-
sitive to the electronic properties of the Si surface and use SHG to study the growth
and thermal desorption of the first two layers of surface oxide, the segregation of less
than 2% of a monolayer of P, and the effect of surface P on the growth of the first layer
of oxide. While the importance of P segregation has been studied for highly-doped (10^{20}/
cm^3) samples[2], it has not been fully appreciated in relatively pure (10^{15}/cm^3) samples.
We also report the first observation of a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern for P on Si(111).

Studies 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 grid analyz-
er for Auger Electron Spectroscopy (AES). The Si(111) wafers (0.010" thick, 10^{15}/cm^3 P-
doped) were supported by Ta clips which also served as electrodes for direct ohmic heat-
ing. For SHG measurements, frequency-doubled Nd^{3+}:YAG laser pulses at 532 nm with 7ns
width and ~ 10 mJ energy were incident at 45° with a 6.2 mm beam diameter. The SH signal
was detected with a photomultiplier tube and processed with gated electronics. Si sur-
faces were cleaned of oxygen by thermal annealing at 1000°C into a 10^{-9} torr vacuum for ~
2 minutes. This treatment left negligible oxygen and only a small amount of carbon (the
ratios of AES peaks were $O_{507}/Si_{92} < 5 \times 10^{-4}$ and $C_{270}/Si_{92} = 1.5\%$). The appearance of
the sharp 7 X 7 LEED pattern upon cooling the sample was taken as a further sign of
nominal cleanliness.

In Fig. 1, we show the SH intensity from the Si(111) surface held at room tempera-
ture and 800°C as we exposed it to 10^{-6} torr of O_2. Previous workers[3], have established
that at room temperature O_2 chemisorbs to Si(111) forming a saturation monolayer in
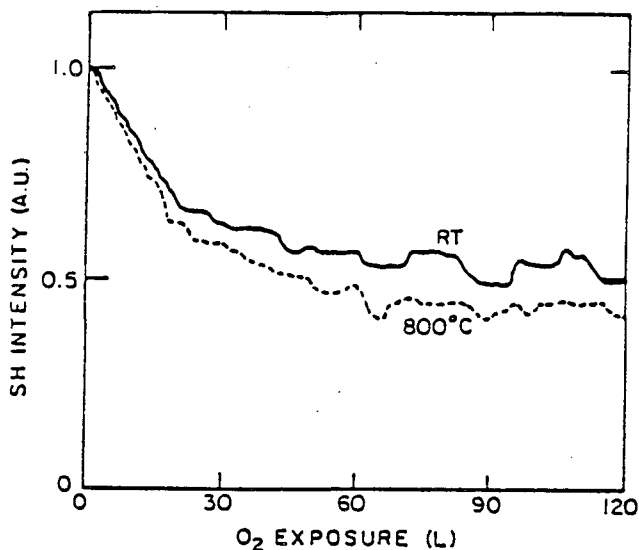
Fig. 1. SHG during oxidation of Si(111) surface at room temperature (RT,——) and at 800°C (---). SH intensities have been normalized to their clean Si levels. 1 Langmuir (L) = 10^{-6} torr-sec.

- 100L. As shown in Fig. 1, the SHG dropped to a saturation level 50% of its clean surface level at ~ 70L indicating the chemisorbed layer was complete. The O_{507}/Si_{92} Auger peak ratio after 120L of O_2 exposure at room temperature was 1.0% and set the scale for a monolayer of O-atom coverage. At increased temperatures, oxygen is known to penetrate the surface to form intermediate Si-O species and stoichiometric SiO_2[4]. For oxidation at 800°C (--- curve), the SHG decreased to a slightly lower saturation level than for the room temperature case. By 30L, the SH was reduced by ~ 50% and AES indicated that there was 1.3 of an O-atom monolayer equivalent on the surface. SHG was relatively insensitive to further oxide growth between 30L and 120L of O_2 exposure over which range AES indicated the surface oxygen increased to 2 monolayer equivalents. A longer O_2 exposure equivalent to ~ 4 monolayers left the SH intensity unchanged. The sensitivity of SHG to only the chemisorbed O-layer and ~ 1/2 layer of subsurface oxide is reasonable as the highly-polarizable metal-like electrons of the 7 X 7 surface contribute strongly to the SH response) and are almost completely quenched by the chemisorption of O. The residual SH signal should not be affected by the growth of an optically thin layer of amorphous SiO_2 as the SH from fused silica is ~ 100 times smaller than the SH from a Si wafer with a native oxide layer.

We also used SHG to observe the thermal desorption or diffusion of O from the Si surface. The cleaned sample was annealed at temperatures between 800°C and 1000°C into 10^{-9} torr vacuum briefly and then exposed to 120L of O_2. One or two minutes after closing the O_2 leak valve, the SH increased to 50% of the clean Si level and then slowly increased to the clean Si level. AES showed there was ~ 1 monolayer equivalent of O on the surface when the 50% level was obtained. While it is impossible with AES to distinguish what percentage of the O-atoms remained below the surface, it is likely that the subsurface oxide

leaves the surface before the chemisorbed species. Using that assumption, SH indicated that the chemisorbed species left the interface ~ 5 times slower than did the subsurface oxide. This result is reasonable considering the larger binding energy of the chemisorbed species. In addition the desorption rate was ~ 10 times slower at 800°C than at 1000°C. The rate of desorption slowed down by an additional factor of ~ 10 starting when the SH reached ~ 85% of that for the clean Si surface. This strongly-adsorbed species accounted for ~ 20% of an O-atom monolayer equivalent. It may be the species discussed in ref. 3; alternatively, it may be an oxide species stabilized by surface phosphorus (see below).

The SHG for a nominally clean Si sample decreased as the temperature was raised. AES indicated that this change was correlated to the segregation of P to the surface at room temperature and its diffusion back into the bulk at elevated temperatures. Because the sample contained $10^{15}/cm^3$ P impurities, the changes in SH could be due to no more than 2% of a P monolayer on the surface. As shown in Fig. 2, the SHG behavior during short thermal annealing cycles of heating at 300°C and 800°C and then cooling to room temperature was reversible for the clean surface but irreversible for the surface predosed with a monolayer of chemisorbed O, even though AES showed that the surface O and P composition was the same before and after the cycle. The latter indicates that the change in SH can not be explained merely by changes in the temperature-dependent index of refraction. The results show that while the diffusion and segregation of P on the clean Si surface is
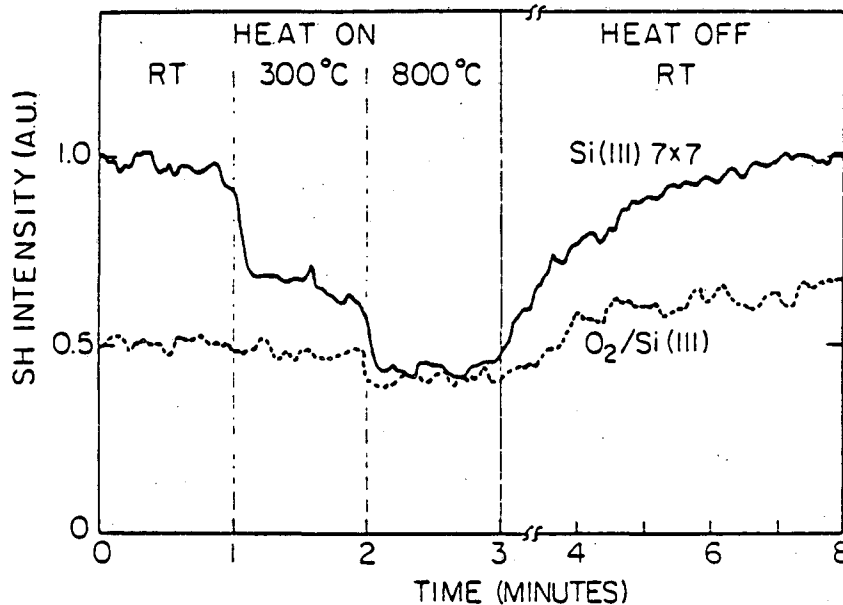

Fig. 2. SHG during thermal annealing cycle: (———) of Si(111) 7 X 7 and (———) of Si(111) with a saturation layer of chemisorbed O prepared by exposing room temperature Si(111) 7 X 7 to 120L of O_2.

reversible, 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 saturation layer of chemisorbed oxygen at room temperature and then immediately heated to 1000°C, the SH increased (consistent with the desorption of oxygen) and then fell (due to the diffusion of P) to the SH level obtained for a clean Si sample heated to 1000°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. Similarly, the low-coverage strongly-adsorbed surface oxide species could have been stabilized by the presence of P. Previous work using Auger Sputter Profiling[2] on heavily ($10^{20}/cm^3$) P-doped $Si-SiO_2$ interfaces found evidence for a strong attractive surface potential for P involving O. 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 X 7 surface of Si(111) has been performed on such samples.

Further oxidation and thermal annealing cycles caused the accumulation of P at the surface and in the near surface bulk. As the surface P concentration increased (P_{120}/Si_{92} AES peak ratio ~ 1.5×10^{-3}), the 7 X 7 LEED pattern became more difficult to see and gradually a sharp $(\sqrt{3} \times \sqrt{3})R30°$ pattern appeared after annealing and then cooling the sample to room temperature. This is the first observation of such a LEED pattern. Because there could be no more than 2% of a P monolayer on the surface, the sharp $(\sqrt{3} \times \sqrt{3})R30°$ pattern is probably not due to a P overlayer (since that would require 1/3 layer of P), but rather due to a P-induced reconstruction of the Si surface atoms. Similar impurity-induced surface reconstructions have been observed on Mo and W (001) surfaces.[5]

In closing, we have studied the growth kinetics of the first two layers of surface oxide and the effect of minute amounts of surface phosphor on the oxidation of Si(111) using a purely optical technique, SHG. While some of these results may not be too surprising because of previous studies using other surface probes, it is surprising that the sensitivity of SHG to the atomic-scale chemistry of the Si surface rivals that of photoemission and is more sensitive than AES in the case of P. The 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.

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5. D. W. Bullett and P. C. Stephenson, Solid State Commun. 45, 47 (1983).