Hydrocarbon reaction with HF-cleaned Si(100) and effects on metal-oxide-semiconductor device quality

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The surface reactivity of hydrogen-passivated, HF-cleaned Si(100) towards hydrocarbon adsorption is examined by surface analysis; most hydrocarbons adsorb on the surface. Dangling bonds formed during thermal processing react with fragmented organic molecules forming SiC. Metal-oxide-semiconductor devices fabricated on contaminated surfaces are degraded, with the degree of degradation depending on the nature of the contaminant.

Integrated processing of wafers and use of chemical passivation layers illustrate two approaches to control of reactive contaminants in future semiconductor manufacturing. Even in an integrated-processing sequence, an imperfect processing ambient would necessitate wafer surface passivation. Passivation layers have to operate within limitations imposed by the nature of the material system, the contaminants involved, and the post-clean process step; their effectiveness needs confirmation in a process-specific manner.

Functionally, a passivation layer has to have limited affinity for impurity species and yet should be removable prior to film growth. HF treatment of Si(100) is used to clean and passivate the surface and the H and F atoms remaining on the surface after etch of the native oxide have important roles in the deposition and growth of high-quality epitaxial Si and SiO$_2$.

The experiments were carried out in a multichamber ultrahigh vacuum (UHV) system that integrates wafer precleaning, film growth, and surface analytical capabilities. Details of the experimental setup and sample preparation have been previously elucidated.

Wafers were loaded into a glove box purged with ultrapure nitrogen (10 ppb purity), etched in a 10% HF solution, and then exposed to hydrocarbons (details below). The samples were then loaded through a load lock into an UHV sample-transfer chamber for analysis. Metal-oxide-semiconductor (MOS) testing was performed on capacitors fabricated by in situ atmospheric pressure thermal oxidation at $\approx 900{\degree}$C, with wafer ramp up in oxygen and ex situ Al-gate and forming gas processing.

Figure 1(a) shows the C 1s x-ray photoelectron spectrum (XPS) for the hydrogen terminated surface (HTS); the carbon level is below the detection limit [$<0.05$ monolayers (ML)]. Thermal desorption (TDS) [Fig. 2(a)] and high-resolution electron energy loss (HREELS) [Fig. 3] spectra show only the presence of $\approx 1.5$ ML of C, bonded as SiH$_2$ and SiH groups. To test the reactivity of the hydrophobic HTS surface, they were individually exposed for 5 min in 1 atm of ultrapure nitrogen to the equilibrium vapor pressure of different organic molecules. The carbon uptake in ML as measured by the relative area under the C 1s (1s) peak in XPS is shown in Fig. 1 for some molecules.
Molecular monolayers/C
formic acid 0.14
valeric acid 0.29
capric acid 0.59
methanol 0.69
n-butanol 0.45
pentanol 1.00
acetic acid 1.20
acetonitrile 0.56
ethyl acetate 0.03

HTS + vol. acid
-292 BINDING ENERGY (eV)
-287

FIG. 1. XPS C 1s spectra from hydrogen-terminated surface (HTS) and
(HTS + valeric acid) samples. No vacuum anneal was carried out. No
measurable C 1s intensity is observed with the HTS surface, showing
the effectiveness of the passivation and ultraclean integrated processing in
contamination control. The accompanying table lists surface carbon cov-
erages (C 1s/Si 2p) for various hydrocarbon contaminants.

ically shifted components in the XPS spectra and the com-
parable peak desorption temperature (≈440 °C) for all the
species studied by TDS, suggests that the first pathway is
more probable. However, there is some evidence for ther-
maxally induced dissociation during heating to process tem-
peratures. This can be seen in Fig. 2 as a general broaden-
ing of the m/e = 15 peak towards higher temperatures [see
also (c) and (d)]. CH, fragments from molecular frag-
mentation could cause this, although for valeric acid it is a
small fraction of the initial coverage.

If hydrocarbons are still at the surface when H passi-
vation is lost via SiH decomposition, direct reaction be-
tween exposed surface sites on the Si substrate and the
residual organic contamination can induce molecular frag-
mentation and formation of chemically bonded impurities.
Surface analysis has been carried out to identify any
products of such reactions. HREELS analysis (Fig. 3) in
the region of Si-H bending vibrations of HTS (lower
curve) shows the presence of dihydride groups after the
HF-cleaning step (the Si-SiH, and Si-SiH2 vibrational losses
are shown). Annealing to temperatures greater than 400 °C
results in loss of the dihydride moieties (Fig. 2) and only
the monohydride species remain on the surface. For the
HTS surface contaminated with hydrocarbons, when an-
nealing is extended to 700 °C (upper curve), reactive in-
teraction between exposed surface sites and the hydrocar-
bon molecule results in SiC formation as evidenced by the
appearance of a peak at the Si-C stretching frequency in
HREELS. The detection of Si—C bonds by HREELS does
not necessarily imply that an identifiable SiC material

phase exists at the surface since the carbon may be prima-
rily in the form of point defects. However, scanning tun-
neling measurements have shown that SiC aggregates can
form quite readily upon annealing to temperatures
around 800–900 °C.

FIG. 2. Smoothed thermal desorption spectra from H-terminated Si(100)
(HTS) and (HTS + valeric acid) samples. The TDS signatures are
shown for (a) H,(m/e = 2), (b) CH,(15), (c) CH,(CH,),(57), and
(d) CH,(CH,),(CO(85). The ramp rate was 10°C/s.

FIG. 3. High-resolution electron energy loss spectra for (bottom) as-
cleaned/HF-dip cleaned Si(100) wafer, (top) hydrocarbon contaminated
wafer after UHV anneal to 700 °C for 10 min. Changes in the Si-H
vibrational spectrum follow from changes in the total surface hydrogen
coverage. The upper spectrum illustrates the formation of SiC moieties.
Figure 4 compares breakdown field strength and high-frequency quasi-static capacitance-voltage (C-V) data for MOS structures fabricated on RCA-cleaned and (HTS + valeric acid) samples. Previously, it has been shown\(^1\) that thermal oxidation in our integrated-processing tool under oxygen ramp-up conditions gives oxides of similar electrical quality for RCA and RCA + HF cleaned wafers, making the present comparison a valid one. Adsorption of valeric acid (0.29 ML) results in a reduction in breakdown field strength by a factor of 2-3, \(\Delta D_d, \) change in the interface trap density \(\approx 100X,\) and \(\Delta V_{fb,} \) change in flatband voltage \(\approx -1\) V. The C-V curves also suggest the presence of a considerable amount of positive fixed charge in the bulk of the oxide, which may be due to the incorporation of the carbon in the oxide. The high \(D_d\) value indicates the presence of a significant number of defect sites at the Si/SiO\(_2\) interface. Together, these results suggest that the carbon is fairly broadly dispersed in the MOS structure during processing.

The data illustrate that significant \((10^{14}-10^{15} \text{ atoms/cm}^2)\) hydrocarbon contamination can cause serious degradation in MOS device quality. The type of hydrocarbon adsorbed determines the extent of degradation. For example, a similar level of propanol adsorption results in \(\Delta D_d = 1.2 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}, \) and a breakdown field strength of 7-10 MV/cm. These values indicate less degradation than for valeric acid. The extent of degradation depends on at least three factors: (i) hydrocarbon sticking probability on the HTS, (ii) its peak-desorption temperature compared to that of H passivation, and (iii) the ease of molecular fragmentation. Organic molecules that (i) exhibit a high sticking probability, (ii) have a desorption temperature that is normally higher than the temperature at which H-passivation is lost, and (iii) fragment easily during thermal processing can be expected to cause the most damage to film electrical quality.

In conclusion, hydrogen passivation of Si(100), which prevents reoxidation of the surface, is not a good passivant against hydrocarbon uptake and SiC defect formation. To serve as a substrate for subsequent film growth, HF-cleaned surfaces should have minimal exposure to hydrocarbon-containing ambient gases. On surfaces contaminated by hydrocarbons, in situ cleaning techniques based on high-temperature vacuum anneals enable only partial removal of the contaminant. SiC moieties are formed during annealing and cause dielectric degradation in MOS structures.

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