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OF SILICON-SILICON DIOXIDE INTERFACE[*]

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ABSTRACT

Conductivity of a silicon-silicon dioxide interface has been measured as a function of temperature. From the data the activation energies of the impurity levels introduced by the various ambient and heat treatments are estimated. Knowledge of surface charge density and carrier mobility is used to calculate the surface parameters. Based on the quenching experiments, a mechanism for the various effects observed has been suggested. Some other electrical properties of the system are discussed in the light of these observations.

I. INTRODUCTION

During recent years the properties of silicon-silicon dioxide inter-
face have been investigated extensively.[1-6] Much of this investigation
was due to the use of oxide for the passivation of silicon surfaces and as
a mask for diffusions in the technology of planar devices. Also, because
of the use of various carrier gases in this field of technology, the effects
introduced by them are included in this study. From a practical point of
view it is necessary to understand the electrical effects produced at a
$Si-SiO_2$ interface, as the development of new devices entirely based on
this system (like the surface field-effect transistor) depends largely on the
understanding of these effects. Electronic properties such as the gain-
bandwidth product and the noise characteristics of these devices obviously
depend on the electrical nature of the system.[7, 8] Experimental and
theoretical investigations into the nature of the interface and the effect of
heat treatments under various ambients have therefore been carried out by
several authors.[9-12]

In the course of our earlier work we observed considerable dependence
of surface properties on various ambient treatments.[12] We measured
surface-charge density and conductivity of the inversion layer formed
under the thermally grown oxide on high-resistivity p-silicon. We reported
that the conductivity varied from $\approx 7 \times 10^{-8}$ ohm^{-1}-cm^{-1} for nitrogen
treatment to $\approx 2 \times 10^{-5}$ ohm^{-1}-cm^{-1} for hydrogen treatment. This depend-
ence of conductivity on ambients can of course be utilized to achieve
control of surface properties desirable for a particular device application.

The present work was undertaken to provide an insight into the mechanism of the conductivity effects produced by the various ambient and heat treatments. We have measured the conductivity of the inversion layer as a function of temperature, and from this data estimated the activation energies of the impurity levels introduced by these treatments. Knowledge of the surface-charge density enables us to draw the energy-level diagram of the oxide-semiconductor system. In some cases the occurrence of the energy levels almost in the middle of the band gap suggests the possibility of these levels acting as recombination centers and noise generators.[13] In the following sections, these results are discussed in detail and a possible mechanism for the various observed effects is suggested.

2. PREPARATION OF DEVICES AND MEASUREMENTS

The method of device preparation has been described in detail in Ref. 12 and will be only briefly outlined here. Wafers of high-resistivity (2000 to 4000 ohm-cm) p-type silicon are lapped, etched, and oxidized in steam for 2 hours at 1000°C. On one side of the wafers windows are etched for phosphorus diffusion to provide electrical contacts with inversion layer under the oxide. The compound $POCl_3$ is used as the phosphorus source and oxygen is used as the carrier gas during the predeposit period. The diffusion is carried out at 900°C for 30 minutes and various ambients are used in this process. The furnace is then allowed to cool to temperatures ≤ 600°C in the respective ambients before the wafers are pulled out. In our study we have used three dry ambients: (a) nitrogren, (b) oxygen and (c) nitrogen + 5% hydrogen. Nitrogen was boiled directly from a liquid nitrogen tank. Ambient (c) was carefully deoxidized and dried. After

diffusion the oxide from the back of the wafers is removed by dissolving it

in HF. The wafers are then given a quick etch in 8:1 $NH_4F:HF$ mixture,

cleaned, dried and aluminum evaporated on the front junctions. The fin-

ished device is shown in Fig. 1.

The devices are then mounted on a copper platform constructed in

a vacuum chamber. The platform is cooled by a copper cold finger pro-

truding outside the chamber. A thermocouple attached to the platform

measures its temperature. The conductance of the inversion layer is

measured at various voltages low enough so as not to affect the properties

of the layer. The geometry of the device (10-mm i. d., 14 mm o. d. in our

case) being known, the surface conductivity can be calculated from these

measurements.

Assuming that a single type of impurity level is present in the

inversion layer, we can express the conductivity as a function of temper-

ature by the following relation:

$$\sigma(T) = \sigma_0(T) e^{-\Delta E/kT}$$

where ΔE is the activation energy, k the Boltzmann constant, T the tem-

perature in degrees Kelvin, and $\sigma_0(T)$ is the known value of conductivity at

some temperature T. In general, σ_0 will be a complex function of temper-

ature. In fact, it will depend on the various scattering mechanism oper-

ating on the carrier mobility in the surface region. Thus the drift mobility

of the carriers in a direction parallel to the surface will depend on temper-

ature through a power law such as $T^{-\alpha}$, where α is a small number. The

mobility will not rise as steeply as in the case of the bulk semiconductor.

The interface being an amorphous boundary, scattering by flaws will be the

primary mechanism for this dependence. In addition to this, the mobility will

also be affected by the transverse electric field due to the presence of the

charge in the surface states.   When Schrieffer-type surface scattering is

assumed , the mobility will be inversely proportional to the electric

field.[14]   If the charge density and hence the transverse electric field

vary with temperature, the mobility will also be affected by them.   On the

whole the effect of these various processes will be to increase $\sigma_0(T)$ as

the temperature is reduced.   But in a temperature range corresponding to

an energy within a few kT's of the activation energy, the exponential term

will dominate the temperature dependence of $\sigma(T)$.   We can therefore

make an approximation and estimate the activation energy from the slope

of the log σ vs $1/T$ plot.   The interpretation of the data for two energy

levels close to each other is difficult, and in such a case we give the acti-

vation energy of the level that seems to primarily determine the properties

of the inversion layer.

3. EXPERIMENTAL RESULTS

The results obtained with the various treatments are described be-

low and summarized in Table I.   In most of the cases we have followed

standard annealing cycle.   After the 60-sec predeposit period the diffusion

is carried out at 900°C in the respective ambients for 30 min.   In the case

of hydrogen treatments after the predeposit, we always introduced nitrogen

for 5 min to sweep away the oxygen from the furnace.   The furnace is then

allowed to cool to different temperatures below 600°C.   In our setup it takes

about 45 min for the furnace to cool to 600°C and as much time to cool from

600°C to 500°C.   We have not made any deliberate attempt to anneal the

devices for longer periods of time at any temperature.

3.1 Nitrogen treatment

For devices treated in nitrogen, the conductivity falls steeply as the temperature is lowered. The activation energy obtained from the log σ vs $1/T$ plot (Fig. 2) for devices pulled out at 600° N (900/600) is 0.39 ± 0.01 eV. We found the activation energy to be lower (=0.36 eV) if the devices are pulled out at a temperature $\leqslant$ 500°C N (900/500). Cooling the devices to room temperature did not make any difference in this value.

To check the possibility of the earlier higher temperature (steam oxidation at 1000°C) having any effect on the device behavior, we carried out the phosphorus diffusion at 1050°C. The device was cooled to 600°C N (1050/600). The activation energy was 0.39 eV. In another batch of experiments we took a number of devices having a different previous history, including multiple heat treatments, and carried out the 900 to 600°C annealing cycle. The activation energy was again 0.39 eV, N (assorted 900/600) but in this case the results were not always reproducible. In the case of the inversion layer formed on low-resistivity (50 ohm-cm) p-silicon, we observed a very small decrease in the conductivity as the temperature was lowered even to liquid nitrogen temperature. Removal of aluminum from the front junction did not make any difference in the values measured above.

3.2 Oxygen treatment

For devices treated in oxygen and cooled to 600°C O (900/600) the activation energy is 0.30 ± 0.01 eV (Fig. 3), and when they are cooled to $\leqslant$ 500°C O (900/500) it is 0.26 eV. Again, the previous history did not matter. In the case of oxygen we suspect two activation energies but from the conductivity measurements it is not possible to establish either their existence or their exact values.

3.3 Hydrogen treatment

We have carried out several types of heat treatments with hydrogen as the ambient. In the first type, hydrogen was introduced in the furnace (at 900°C) for 10 min and 30 min and during rest of the time nitrogen. The devices were pulled out at 600°C. The activation energy in both cases was 0.38 eV H (900H/600N), similar to that of the nitrogen case. For devices cooled to 600°C in hydrogen H (900/600), the value was 0.16 eV. When the devices were cooled to 500°C H (900/500) the activation energy was less than 0.1 eV. In this case the sign of the coefficient of the electrical conductivity as a function of temperature also changed from plus to minus. The same result was obtained for devices cooled in nitrogen from 900°C to 600°C but in hydrogen from 600° to 500°C H (900 to 600N/600 to 500H), and for devices quenched in hydrogen at 600°C. The conductivity at liquid-nitrogen temperature was ≈ 2.5 the conductivity at the room-temperature value. For these devices we also measured carrier mobility as a function of temperature.

The results for hydrogen treatments are shown in Figs. 4 through 7. The flip-over of the sign of the conductivity coefficient probably occurs at a temperature ≈ 570°C, i.e., devices pulled out of the diffusion furnace at a temperature > 570°C have a plus sign and < 570°C have a minus sign. Hydrogen treatment also reduced the diode reverse current.

4. CALCULATIONS OF SURFACE PARAMETERS

In this section we calculate the various parameters that occur in the description of the electrical properties of the inversion layer. In Table II the data on the surface charge density, the effective carrier mobility, and

the impurity levels (ΔE) are compiled. In our case, because of the high surface charge density and the high resistivity of the substrate, we can easily calculate the surface potential ϕ_s from the knowledge of the charge density Q_s.[15] The surface potential is given by

$$Q_s = 2\ qn_i L_D\ \exp(\tfrac{1}{2}\ U_s)$$

where q is the electronic charge; n_i the carrier density in the intrinsic material; L_D the Debye length; and U_s the surface potential in units of kT/q (i.e., $U_s = q\phi_s/kT$) measured with respect to the bulk. In Fig. 8 we have plotted Q_s as a function of U_s at 300°K. Also, from the knowledge of Q_s we can calculate the electric field E_s acting on the carriers. It is given by

$$Q_s = \frac{\epsilon}{4\pi}\ E_s\ ,$$

ϵ is the dielectric constant of the semiconductor. From ϕ_s and E_s we estimate the "thickness" t of the inversion layer in which the charge is confined to move, i.e., $t = \phi_s/E_s$.

Knowing the impurity levels, the surface potential, and the bulk resistivity, we can draw the complete energy-level diagram of the surface. This diagram for a device treated in nitrogen is shown in Fig. 9.

It is interesting to compare the measured values of the effective carrier mobility μ_e with the one theoretically derived. Calculation of the mobility as a function of transverse electric field based on the Schrieffer-type scattering has been done by Root and Vadasz.[16] These values, along with other parameters, are given in Table III. Whereas the agreement between the theoretical and experimental values of mobility for the hydrogen and the oxygen treatments can be considered to be reasonable in a general way--in view of the various approximations made in both the theoretical derivations and experimental measurements--the results do not tally in the nitrogen case. It seems that this treatment introduces trapping centers with a large capture cross section, thus reducing the life-time of the carriers and hence the effective mobility.

Because the energy levels introduced by the nitrogen and oxygen treatments are deep lying, they can be the sources of generation-recombination noise.[13] Also because these levels are deep levels, thermal fluctuations will lead to random changes in the carrier-densities; these could be other sources of noise in devices having oxide on the surface.[17] The presence of surface traps in the nitrogen treatment can be one of the sources of low-frequency noise in these devices. On the other hand, devices treated in hydrogen H (900/500) exhibit the typical T^{-a} law for the mobility. These devices should also be comparatively quieter.

5. DISCUSSION

Several things are known to happen at the oxide-semiconductor interface as a result of diffusions and heat treatments. Atalla and Tannenbaum[18] and Grove, Leistiko, and Sah[19] have studied the problem of impurity pile up and depletion from the interface. Here the case of depletion of boron from the interface treated under hydrogen seems to be interesting. Zaininger and Warfield have felt it necessary to postulate the presence of trapped charge in the oxide to explain some of their results with the hydrogen treatment.[20] Recently, Seraphim et al. have put forward the theory of the formation of oxygen-ion vacancies in the oxide to explain their results on the passivation of silicon surfaces by the oxide.[21] While considering these hypotheses we should also bear in mind the possibility of the surface's picking up phosphorus or other donor-type impurities from the etchants. The pile up of these impurities combined with the depletion of boron from the interface can give rise to effects that could be significant in the case of high-resistivity silicon. In this context we should also remember some of the well-known effects of heat treatments in the bulk semiconductor. We would like to elaborate on this point.

A number of workers in this field have studied the diffusion reactions, kinetics, and precipitation of oxygen in silicon.[22] It has been demonstrated that when silicon crystals containing oxygen are heated in the temperature range 450° to 500°C, donors are formed that disappear when the temperature is again raised above 500°C. Recently Corbett et al.[23] have found the appearance and disappearance of several infrared bands as a consequence of heat treatments in the temperature range 300° to 500°C. On the basis of their results they propose models for the nucleation and growth of oxygen agglomerates in the vicinity of a lattice vacancy. The nucleus of this process could be a substitutional oxygen atom. On the other hand, Bemski and Dias have studied the quenched-in defects in p-type silicon and report a high diffusion constant for the donor-like defect.[24] From this they conclude that the defect is interstitial in silicon. Whether or not these mechanisms govern the formation of defects and agglomerates at the silicon-silicon dioxide interface, a few conclusions can be easily reached from these observations.

That the heat treatment of silicon at a temperature ≈ 500°C marks a transition point in the properties of the material is clear from the above. Also, the change in the electrical properties of silicon can very well be ascribed to the precipitation of oxygen and formation of various complexes with silicon at different temperatures. Interaction of oxygen with both the dislocations and the impurities in the semiconductor can also occur and give rise to several effects. These phenomena seem to be striking in the context of the present work. From this it appears that without assigning any special attributes to the oxide, an explanation for the results reported here could be sought in the kinetics of precipitation and formation of agglomerates. To illustrate the assumption we can refer to the hydrogen treatments. Devices

pulled from a furnace at 600°C show a temperature dependence dominated by the presence of deep energy levels. This could be due to the formation of some Si-O complex in the temperature range 600° to 500°C. On the other hand, wh̄ṇ hydrogen is present in this temperature range, the devices show a rise in conductivity with lowering temperature. Apparently the formation of complexes is suppressed by the presence of hydrogen in this temperature range. The occurrence of various activation energies can be considered to be due to the formation of several different SiO_x complexes in the presence of high or low oxygen concentrations. Further, the oxide-semiconductor interface, being a boundary of two elastically dissimilar materials, will give rise to strain fields that can affect the kinetics of these processes in this region. In fact, it seems to be a natural site for the precipitation and formation of various defects and complexes. In addition, if the quenched-in defects are interstitials they will rapidly migrate to the surface and give rise to various effects. On the basis of the present data it is not possible to propose any definite models that will explain the detailed nature of these complexes and the exact role they play in determining the properties of the interface. Probably measurement of a more basic parameter, like the Hall coefficient, would yield more information about the physical nature of the interface.

6. SUMMARY

The effect of heat treatments in various ambients on the properties of silicon-silicon dioxide interface was studied. From the temperature dependence of the surface conductivity the activation energies of the levels introduced by these treatments were calculated.

From the knowledge of surface densities and activation energies, the energy-level diagrams of the interface were prepared.

The electrical properties of the inversion layer were discussed in the light of these results.

On the basis of the results of the quenching experiments, a tentative general theory involving precipitation and formation of Si-O complexes at the interface is suggested.

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FOOTNOTES AND REFERENCES

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†I. A. E. A. Fellow from Atomic Energy Establishment Trombay, Bombay, India.

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Table I. Activation energies.

Device-Treatment Conditions	$\Delta E(eV)$	$\frac{d\sigma}{dT}$
Nitrogen		
N(900/600)[a]	0.39	+
N(900/500)	0.36	+
N(900/25)	0.36	+
N(1050/600)	0.39	+
N(Assorted 900/600)	0.39·	+
Oxygen		
O(900/600)	0.30	+
O(900/500)	0.26	+
O(900/25)	0.26	+
O(Assorted 900/600)	0.30	+
Hydrogen		
H(900H, N900/600)	0.38	+
H(900/600)	0.16	+
H(900/500)	< 0.1	-
H(N900/600, H600/500)	< 0.1	-
H(900/25)	< 0.1	-
H(900/600) Quenched in hydrogen	< 0.1	-

[a]Annealing range given in °C.

Table II. Properties of the inversion layer.

Device-Treatment Conditions	$\sigma_0(300°K)$ (ohm^{-1}-cm^{-1})	$Q_s(300°K)$ (C/cm^2)	$\mu_e(300°K)$ (cm^2/V-sec)	ΔE (eV)
N(600)[b]	7.5×10^{-8}	7.5×10^{-8}	1.0	0.39
O(600)	2.0×10^{-6}	2.5×10^{-7}	8.0	0.30
H(500)	1.8×10^{-5}	3.0×10^{-8}	600	< 0.1

[b] Temperature in °C at which the devices were pulled out of the furnace.

Table III.   Surface parameters(300°K).

Device-treatment conditions	Q_s (C/cm^2)	E_s (V/cm)	ϕ_s (V)	t (Å)	μ_e(expt.) $(cm^2/V\text{-sec})$	μ_e(theor.) $(cm^2/V\text{-sec})$
N(600)	7.5×10^{-8}	7.0×10^4	0.45	650	1.0	75
O(600)	2.5×10^{-7}	2.4×10^5	0.52	220	8.0	20
H(500)	3.0×10^{-8}	2.8×10^4	0.40	1400	600	190

FIGURE CAPTIONS

Fig. 1. Typical silicon-silicon dioxide surface field-effect device.

Fig. 2. Surface conductivity as a function of temperature for devices treated in nitrogen (900/600).

Fig. 3. Surface conductivity as a function of temperature for devices treated in oxygen (900/600).

Fig. 4. Surface conductivity as a function of temperature for devices treated in hydrogen (900/600).

Fig. 5. Surface conductivity as a function of temperature for devices treated in hydrogen (600/500).

Fig. 6. Surface conductivity as a function of temperature for devices treated in hydrogen (900/500).

Fig. 7. Carrier mobility as a function of temperature for devices treated in hydrogen (900/500).

Fig. 8. Surface potential as a function of surface-charge density (300°K).

Fig. 9. Complete energy-level diagram of $Si-SiO_2$ interface for device treated in nitrogen (900/600).

$$\frac{D-d}{2}$$

Al

SiO$_2$

N$^+$-silicon

p-silicon

n-on-p inversion layer

∅

MUB-5103

Fig. 1

Fig. 2

Fig. 3

CONDUCTIVITY σ_s (ohm^{-1}-cm^{-1})

10^{-5}

10^{-6}

10^{-7}

10^{-8}

#H(900/600)

SLOPE
0.084 eV

3   4   5   6   7   8   9   10

1000/T (1/°K)

MUB-5104

Fig. 4

Fig. 5

MUB-5105

Fig. 6

Fig. 7

Fig. 8

MUB-5106

$E_i - E_f = 0.15 eV$

$E_f - E_{is} = 0.45 \quad (=\phi s)$

$E_{cs} - E_d = 0.39$

$E_c - E_v = 1.10$

p Si ($\rho = 2500$ ohm-cm)

MUB-5102

Fig. 9