THE EFFECTS OF CO, WATER VAPOR AND SURFACE TEMPERATURE ON
THE CONDUCTIVITY OF A SnO_2 GAS SENSOR

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It is shown that the conductivity of a SnO_2 gas sensor de-
pends on the concentration of CO and H_2O in the atmosphere
in which it is placed. The experimental data can be ex-
plained in a consistent manner by hypothesizing that 1)
adsorbed oxygen depletes the surface electron concentration
and therefore decreases the conductivity; 2) adsorbed water
causes electrons to accumulate at the surface and therefore
increases the conductivity; 3) CO increases the conductiv-
ity by removing adsorbed oxygen by reacting with it to form
CO_2; and 4) adsorbed water catalyzes the CO to CO_2 reaction.

Key words: tin oxide, gas sensor, oxygen adsorption,
carbon monoxide adsorption, water adsorption.

Introduction

It is well known that some gases are adsorbed on the
surface of the metal oxide semiconductors, ZnO and SnO_2,
[1-4] and that the semiconductors are n-type. They are n-
type because they have an excess cation concentration.[1]
The adsorbed specie can either decrease the electrical
conductivity as it does in the case of oxygen adsorbed on
zinc oxide,[1-3,5] or increase the conductivity as it does

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in the case of hydrogen adsorbed on zinc oxide.[5]

It is thought that oxygen decreases the conductivity because it becomes chemisorbed by capturing donor electrons thereby decreasing the carrier concentration.[1,5]   One piece of evidence which supports this hypothesis is that the oxygen has a greater effect when it is adsorbed on the zinc surface of ZnO (the (0001) surface) where the dangling zinc bonds[6] more readily give up their valence electrons. Oxygen captures electrons because its work function is greater than the work function of the semiconductor. The captured electrons and the positive depletion layer charge create a potential which bends the energy bands (see Fig. 1)
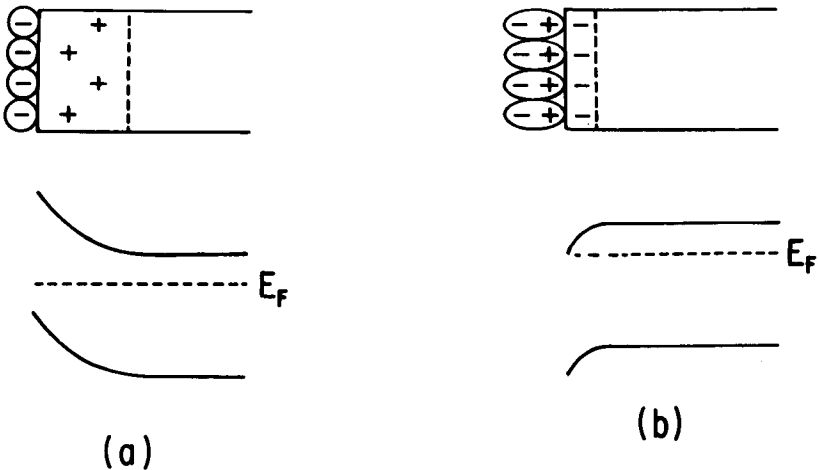

E_F

(a)   (b)

Fig. 1 Simple energy band diagrams for a) the surface of an n-type semiconductor in which the surface electron con- centration has been depleted by an electron transfer to an adsorbed atom, and b) the surface of an n-type semiconduc- tor in which electrons are attracted to the surface by the preferential alignment of molecular dipoles.

thereby allowing the Fermi energies to equilibrate. A pos-
sible explanation for the increased conductivity of ZnO
when it is exposed to hydrogen is that the oxide is a Lewis
acid[4,7,8] and accepts electrons from the hydrogen. That
this is the mechanism is made more plausible by the fact
that the hydrogen has a more pronounced effect when it is
exposed to the oxygen surface (the (0001) surface)[5] where
the oxygen dangling bonds[6] more readily accept electrons.
The bands are bent such that the surface electron density,
and therefore the surface conductivity, increases. As
seen in Fig. 1b the same effect could be obtained if polar
molecules are adsorbed such that the positive charge of
the double layer is in contact with the surface of the
semiconductor. This would cause electrons to accumulate
at the surface.

When the adsorbed gases are removed, as for example
oxygen being removed by reacting with a reducing gas, the
conductivity will change. This conductivity change can be
used to detect the presence of a reducing gas as it is in
the Taguchi gas sensor, (TGS).[9] The working element of
the TGS is an n-type polycrystalline SnO$_2$ film that has
been sintered onto a ceramic tube ~1cm long and 2.5mm in
diameter, and whose conductivity increases when it is ex-
posed in air at atmospheric pressure to a reducing gas.

We are in the unsatisfactory position of not knowing
how these elements are made -- we only know that they are
made by a proprietary process in such a way that their
conductivity is affected by the presence of a reducing
gas. Therefore we must accept the SnO$_2$ as a given quan-
tity, and examine the effects of changing the atmosphere
in which it operates.

In this paper we examine the changes of the conduc-
tivity of the TGS when it is exposed to different concen-
trations of carbon monoxide and water vapor with the goal
of trying to determine if the TGS can be used as a CO
detector. Because the device characteristics vary greatly
from device to device the emphasis of this paper will be
on trends as opposed to quantitative results.

Experimental Procedure

    The experimental setup is shown in Fig. 2. The circuit
voltage, V_C, was applied across the TGS and a 4040 ohm load
resistor using a PVT-30 variac and a TR-3 transformer. The
primary dependent variable, the load voltage, V_L, across
the load resistor, R_L, was measured with an HP model 4000 D
voltmeter. Changes in V_L are synonymous with changes in
the conductivity of the TGS because an increase in the con-
ductivity will produce an increase in V_L. Therefore the
terms will be used interchangeably.

    R_L was chosen to maximize the sensitivity of V_L to
changes in the conductivity of the element (small R_L),
while at the same time not allowing the circuit voltage to
produce excessive I^2R heating in the element (large R_L).
It was decided that the maximum amount of circuit voltage
heating should be no larger than the heater voltage heating
when V_H = 1 V and V_C = 100 V. Since the heater voltage
heating at V_H = 1 V was ~0.6 joules, R_L should be ~4000 ohms
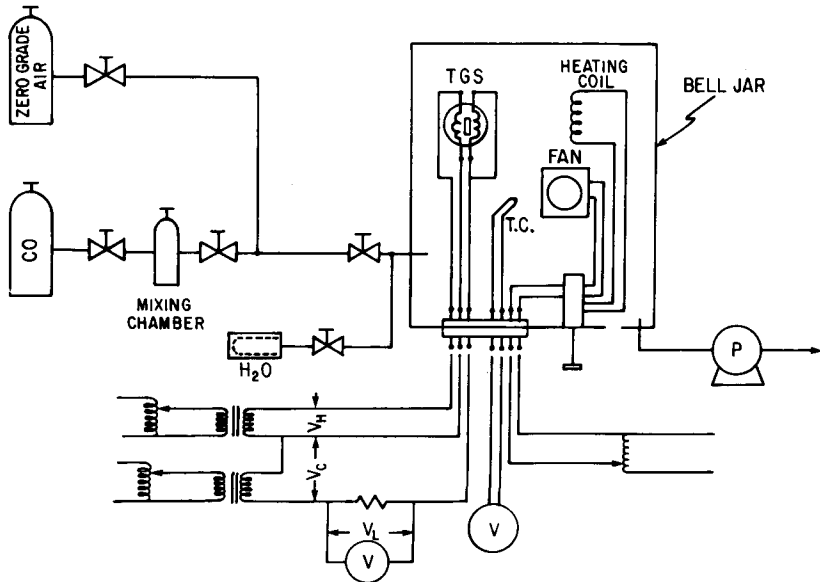because under maximum loss conditions (V_L = 50 V), the cir-

Fig. 2   Schematic for the experimental setup.

cuit voltage heating would be 0.625 joules. At R_L = 4000
ohms the sensitivity of V_L to conductivity changes in the
element is still sufficient because V_L ranged from 60 V
(element resistance of 2.7×10^3 ohms) to 1 V (element re-
sistance of 4×10^5 ohms). Most of the measured voltages
were less than 25 V so that the heating from the circuit
voltage was not considered to be qualitatively important.
It should also be mentioned that heating the SnO$_2$ element
did not degrade it because, it, as all detectors must,
gave reproducible results under repeated testing.

The temperature of the TGS was controlled by applying
a heater voltage, V_H, across a resistor imbedded in it.
The heater voltage was controlled by a PVT-31 variac and
a TR-31 transformer. The temperature of the TGS was
measured as a function of V_H for values of V_H from 0-2 V
using a copper-constantine thermocouple, and it was found
to obey the approximate equation T = 140 V_H + 20°C where
V_H is in volts. There was no V_C during these measurements.
Gases were bled into the bell jar at various concentrations
and were heated by a nichrome wire heater to temperatures
as high as 80°C and circulated by a fan. The water content,
W.C., of the air was measured by placing a YSI dew point
hygrometer in the bell jar and determining the relative
humidity, R.H., as a function of the amount of water in
the water chamber. It was found that one ml of water cor-
responded approximately to 100% R.H. at room temperature.
The ambient gas temperature was monitored with a copper-
constantine thermocouple. It was found that the power
used to heat the TGS did not noticeably affect the ambient
temperature.

The sequence of events for one set of measurements
was as follows. The TGS was hooked up, and the water was
loaded into the water capsule with a microliter syringe.
The bell jar was partially evacuated with a mechanical pump
and V_L was measured as a function of V_H at different pres-
sures. Next the vacuum system was pumped down to a pres-
sure of twenty microns. While the system was being evac-
uated, AIRCO research grade CO was bled into the mixing
chamber and mixed with AIRCO zero grade air to obtain the
desired concentration. The concentration was measured in
ppm with an ESI ecolyzer. The gate valve was closed and
the test gas was allowed to flow into the bell jar until
it reached a pressure of one atm., and then the water was

evaporated from its chamber by passing current through the
heating coil wrapped around it. V_L was measured as a func-
tion of V_C for a fixed V_H, and then V_H was changed and the
process was repeated. After V_H had been changed a fixed
number of times the test gas was raised to a higher temper-
ature using the nichrome heater and the entire process was
repeated. This was done for a number of ambient tempera-
tures. In all instances the measurements were made after
the steady state had been reached. The time it took to
reach the steady state varied, but it was never more than
ten minutes.

Experimental Results

In Fig. 3 V_L is plotted as a function of the total am-
bient pressure for two different ambient temperatures and
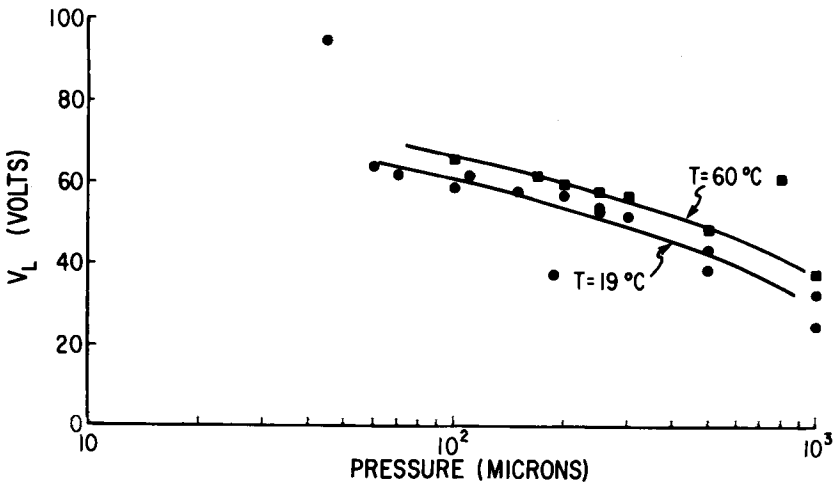for $V_H = 1.0$ V and $V_C = 100$ V. The curve for T = 60°C has

Fig. 3   The load voltage, V_L, plotted as a function of the
pressure when the ambient temperature is 19°C and 60°C, and
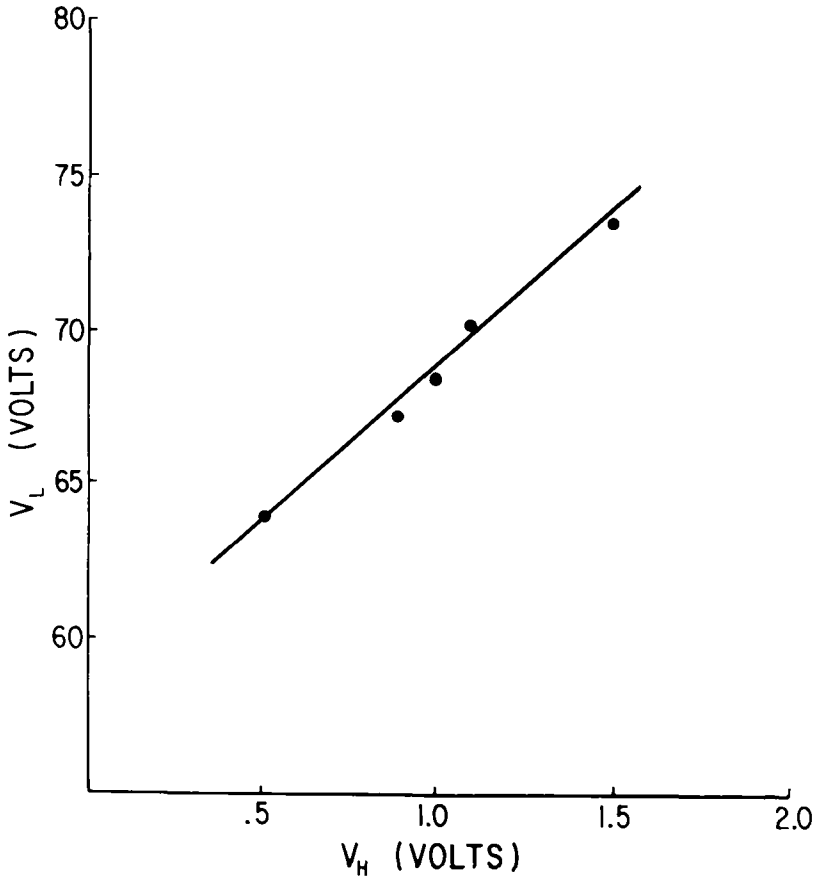$V_H = 1$ V and $V_C = 100$ V.

Fig. 4 V_L plotted as a function of the heater voltage, V_H, when the pressure is 100 microns and V_C = 100 V.

larger V_L values than the curve at 19°C and V_L increases as the pressure decreases. This is the only figure that will exhibit the effects of changing the ambient temperature be- cause the effects produced by changing it are similar to the effects produced by changing V_H. In the figures that follow the ambient temperature is room temperature.

The effect of reducing the pressure and increasing the temperature is also displayed in Fig. 4, where the V_L vs. V_H curve is plotted for the case when P = 100 microns and V_C = 100 V. The value of V_L increases approximately linearly with V_H.
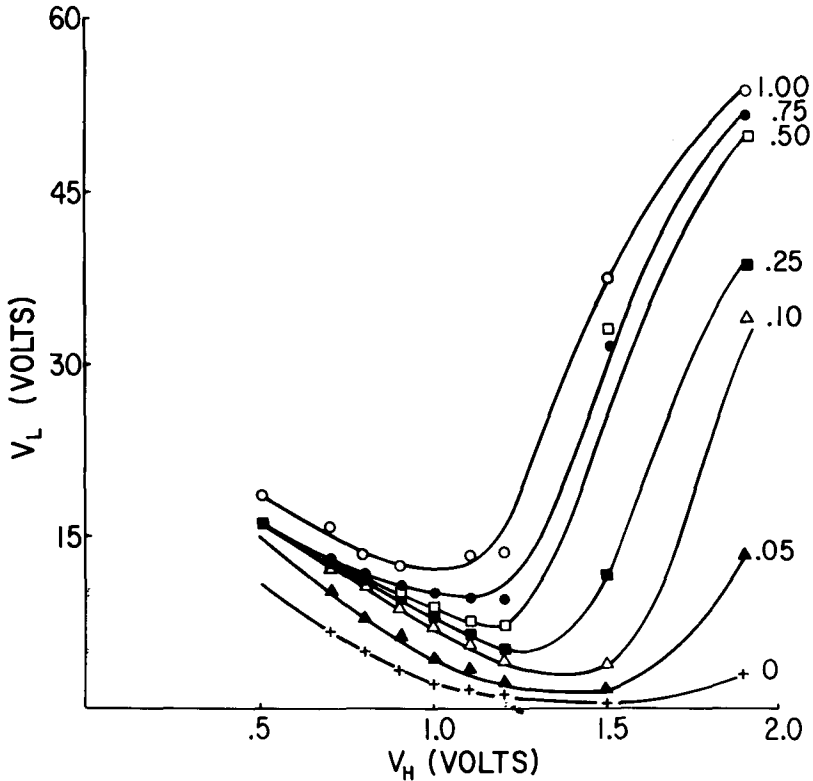
Fig. 5 V_L plotted as a function of V_H for various water contents, W.C., (in ml) when the pressure is 1 atm and $V_C = 100$ V.

However, this linear relationship does not exist when the TGS is exposed to the atmosphere, and, as seen in Fig. 5, the V_L vs. V_H relationship is particularly nonlinear when water vapor is present. These curves were determined for $V_C = 100$ V and there was no CO present. For all values of V_H, V_L increases with the water content. Also, all curves have a similar shape in that they initially decrease and then begin to increase with V_H in the vicinity of $V_H \sim 1$ V. V_L varies more rapidly with V_H and the minimum moves to lower values of V_H as the water content increases.

The conductivity of the TGS is also a function of V_C and the CO concentration. This is illustrated in Fig. 6,
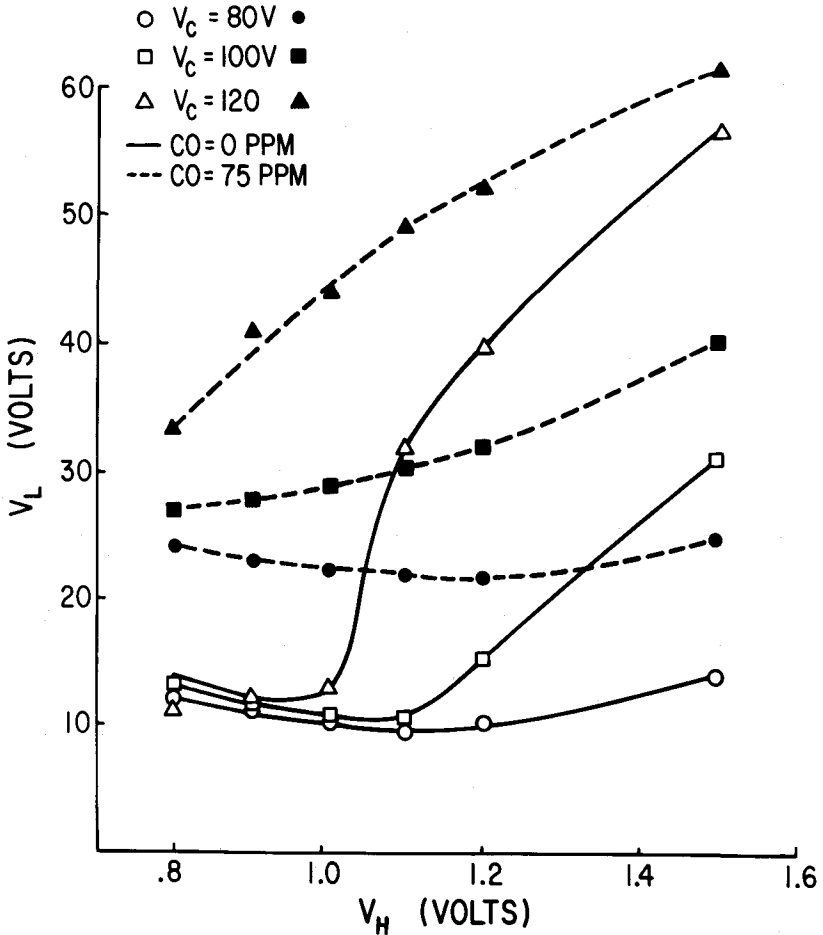
Fig. 6 V_L plotted as a function of V_H for V_C = 80, 100 or
120 V and the CO concentration equal to 0 or 75 ppm when
W.C. = 0.5 ml.

where V_L is plotted as a function of V_H for three different
values of V_C, two different values of CO concentration, and
the W.C. was equal to 0.5 ml. V_L does not increase propor-

tionately with V_C, as it would in the absence of any adsorp-
tion. When there is no CO present, V_L decreases slowly with
increasing V_H for all three values of V_C until $V_H \sim 1$ V.
For larger values of V_H, V_L increases with the most rapid
increase being for $V_C = 120$ V. The curves with correspond-
ing values of V_C have larger V_L when 75 ppm of CO are pre-
sent. This set of curves follows approximately the same
trends as the curves with no CO present with the major ex-
ception being that there is no shoulder in the $V_C = 120$ V
curve.

That both H_2O and CO affect the conductivity of the
TGS is illustrated in Fig. 7, where V_L is plotted as a func-
tion of W.C. for different CO levels in Fig. 7a, and the
same points are replotted in Fig. 7b where V_L is plotted as
a function of CO concentration for different H_2O levels. In
many instances a data point was measured more than once, but
only the average value is plotted to reduce the busyness of
the figures. It is seen that V_L increases with the W.C. up
to W.C. $\sim .25$ ml at which point it increases only slightly
with increasing W.C. Also, the initial increase in V_L is
larger for larger values of the CO concentration. At all
but the lowest values, V_L increases with increasing CO con-
centration with the most rapid increases occurring for CO
concentrations greater than 75 ppm. Both figures show that
there is an anomalous decrease in V_L when the CO concentra-
tion is 5 ppm.

Discussion

It will be shown that the experimental data can be
explained in a consistent manner by hypothesizing that 1)
adsorbed oxygen depletes the surface electron concentration
and therefore decreases the conductivity of the TGS; 2) ad-
sorbed water causes electrons to accumulate at the surface
and therefore increases the conductivity; 3) carbon monoxide
increases the conductivity by removing adsorbed oxygen by
reacting with it to form carbon dioxide; and 4) adsorbed
water catalyzes this reaction.

There is considerable evidence in the literature for
similar materials that suggests these hypotheses are cor-
rect. It has already been pointed out in the Introduction
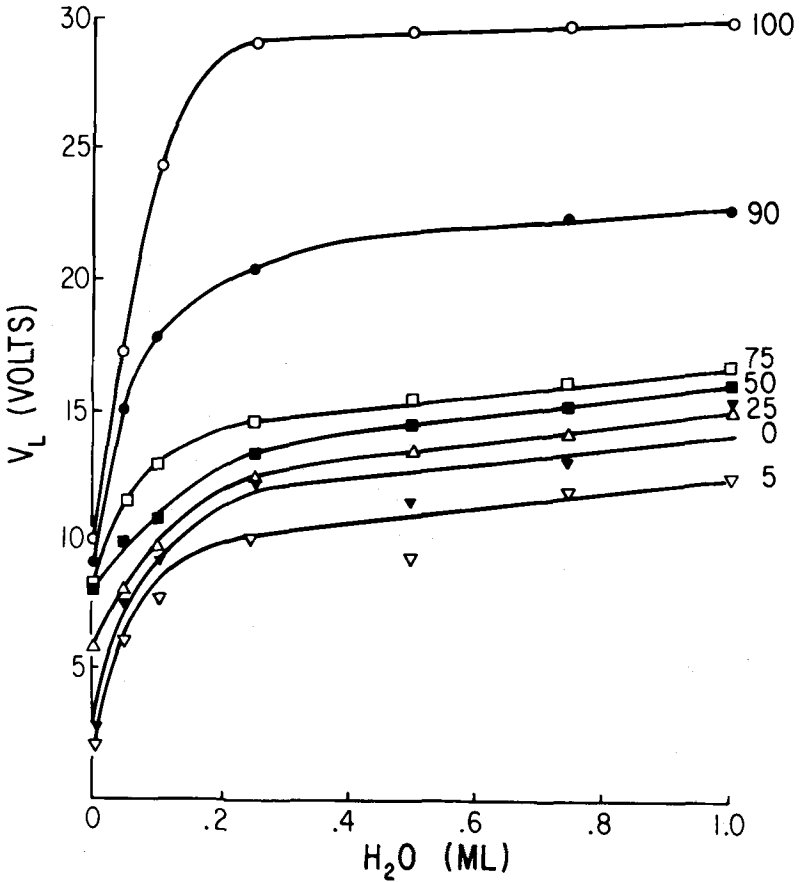that there is much experimental evidence that chemisorbed

Fig. 7 V$_L$ plotted as a function of a) W.C. for various CO concentrations and, b) (see next page).

oxygen reduces the electron concentration on the surface of ZnO.[1-3,5] It has been reported that water increases the surface electron concentration particularly on the surface
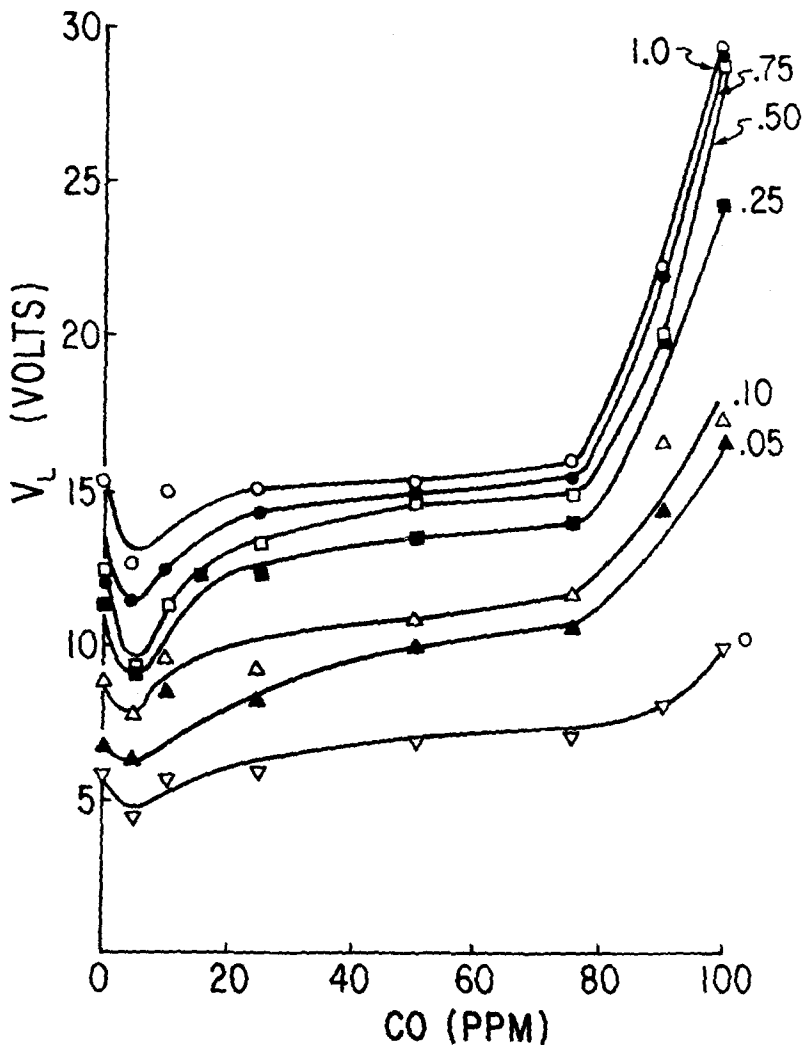
Fig. 7 V_L plotted as a function of b) CO concentration for various W.C., when $V_C = 100$ V and $V_H = 1.0$ V.

of germanium.[10] It has also been shown that CO is not adsorbed but reacts with the adsorbed oxygen on the surface of SnO_2[11] and ZnO.[12] No evidence was found that adsorbed water catalyzes the oxidation of CO to CO_2, but there is evidence that the SnO_2 surface catalyzes this reaction, [11,13] and it has been suggested that hydroxyl groups play an important role in the catalysis.[11]

We will now attempt to show that our experimental re-
sults are consistent with the above hypotheses by first
examining Figs. 3 and 4. Reducing the pressure increases
the conductivity of the TGS and therefore V_L because some
of the adsorbed oxygen desorbs at the lower pressure. The
conductivity also increases when the ambient temperature is
increased because some of the adsorbed oxygen is desorbed
at the higher temperature. If no desorption did occur one
would expect the conductivity to decrease as the semicon-
ductor is in its exhaustion temperature (constant carrier
concentration) region, and the mobility decreases with in-
creasing temperature. The increase in the conductivity with
increasing V_H at P = 100 microns is also due to oxygen being
desorbed at higher temperatures.

No mention was made of water for the low pressure exper-
iments because it has been shown that water is desorbed upon
evacuation. However, it has been shown that water is ad-
sorbed on the surface of SnO$_2$ at room temperature and atmos-
pheric pressure.[11] As seen in Fig. 1b, adsorbed water
molecules will increase the conductivity of the TGS if the
preferential alignment of the dipoles causes electrons to
accumulate at the surface. On the other hand, when water
is thermally desorbed the number of accumulated electrons,
and therefore the conductivity, will decrease. If the ef-
fect of thermally removing water is greater than the effect
of thermally removing oxygen the net effect will be a con-
ductivity decrease. We suggest that this is the reason why
V_L initially decreases with increasing V_H as is shown in
Fig. 5. V_L eventually begins to increase with V_H because
the effect of boiling off the oxygen eventually becomes
more pronounced as the adsorbed water becomes depleted.
This explanation is plausible because polar molecules tend
to be physisorbed instead of chemisorbed and therefore are
bound less tightly to the surface.[14] Thus they would boil
away more easily. This idea is supported experimentally by
Thronton and Harrison[11] who found that much of the adsorb-
ed water was thermally removed at 57°C and all of it was
removed at 200°C.

That gases are adsorbed is also supported by the fact
that V_L does not increase proportionately with V_C. Since
adsorbed gases affect the surface potential, and therefore
the conductivity, it seems reasonable to expect that alter-
ing the surface potential by altering the circuit voltage

should also affect the number and relative concentration of adsorbed molecules. The change in the number and relative concentration of the adsorbed molecules would then be reflected in the nonlinear changes in V_L with V_C. For example, increasing V_C could increase the amount of adsorbed oxygen which would decrease the conductivity of the TGS and therefore retard the increase in V_L.

The initial rapid increase in the conductivity of the TGS and subsequent leveling off at W.C. ~ 0.25 ml seems to indicate that the sites where water can be adsorbed become saturated at relatively low surface concentrations. However, this water appears to play a crucial role in catalyzing the reaction of CO and oxygen to form CO_2. Thornton and Harrison [11] have proposed a specific mechanism for this reaction based on their transmission infrared data. They suggest that CO is attracted to a hydroxyl group because CO produces a small shift in the OH stretching frequency. The CO molecule forms a unidendate ($-O-CO_2$) carbonate by nucleophillic attack of the neighboring oxygen atom. The CO_2 molecule is boiled off and the original surface structure is formed by an oxygen atom moving to the oxygen site made vacant by the formation of CO_2. We conjecture a similar mechanism which differs only in that a hydroxyl group has been replaced by an adsorbed water molecule. The four reactions are shown in Fig. 8. These reactions can be no more than a conjecture since we had no way of determining if there were any OH groups on the surface. It is equally likely that a water molecule is adsorbed at a site neighboring an OH group and this water molecule then "sensitizes" the OH group so that it is a more effective catalytic site.

More studies will have to be made to determine what the precise mechanisms are. More studies will also have to be made in order to understand why there is an initial decrease in the conductivity of the TGS when it is exposed to 5 ppm of CO and why the rate of change in the conductivity with the CO concentration greatly increases at CO concentrations in excess of 75 ppm.

Conclusions

The conductivity of the polycrystalline SnO_2 TGS depends on the atmosphere in which it is placed because it adsorbs
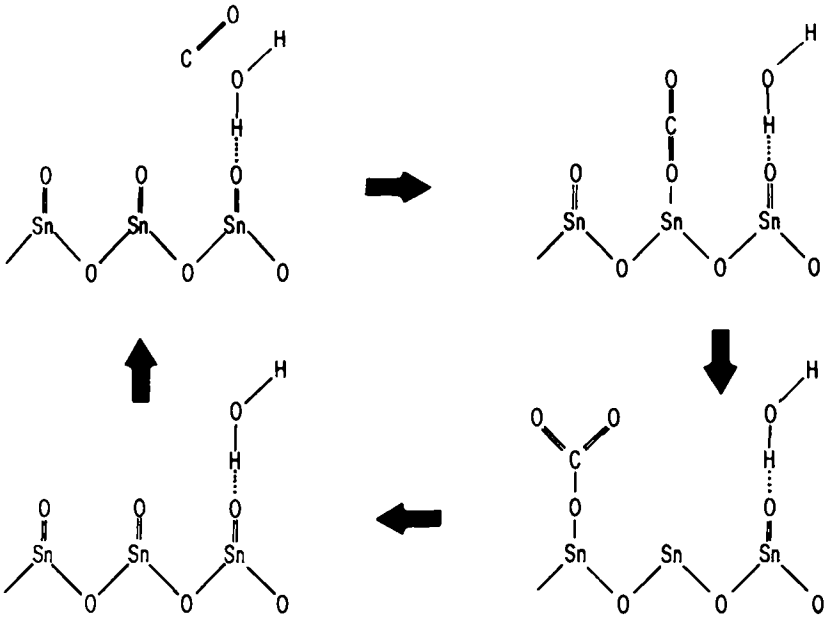
Fig. 8 A possible mechanism displaying how water adsorbed on the surface of SnO$_2$ catalyzes the oxidation of CO to CO$_2$.

gases, and the different adsorbed species affect the conductivity differently. It is suggested that adsorbed oxygen reduces the conductivity by depleting the surface electron concentration through electron capture. This suggestion is based on the experimental evidence that the conductivity increases as the pressure decreases, and that the conductivity increases at low pressure as the surface temperature of the TGS increases. It is also shown that water vapor increases the conductivity, and it is hypothesized that the conductivity increase is produced by surface electron accumulation resulting from the preferential alignment of the water dipoles. This hypothesis is based on the experimental observations that water vapor increases the conductivity, and that it appears to thermally desorb relatively easily. It is also hypothesized that carbon monoxide increases the conductivity because it removes adsorbed oxygen by reacting with it to form carbon dioxide, and that adsorbed water cat-

alyzes this reaction. This is based on the work of others and the experimental evidence that carbon monoxide increases the conductivity, and that the conductivity increases are much larger when water vapor is present. That adsorption does occur is also supported by possible changes in the concentrations of the adsorbed species when the surface potential is changed by changing the circuit voltage. This is based on the experimental evidence that the conductivity of the TGS changes as the voltage across it changes and the changes are different at different temperatures and different atmospheric compositions.

The TGS can be used to detect carbon monoxide because the conductivity of the TGS increases when CO is present. The TGS is a more effective CO sensor when the room temperature relative humidity is greater than 25% because the change in the conductivity with the CO concentration is larger and the conductivity, which is very sensitive to the water vapor concentration below 25% R.H., is almost independent of the water vapor concentration above 25% R.H. The change in the conductivity with the CO concentration is also greater when the CO concentration exceeds 75 ppm.

This paper deals only qualitatively with the conductivity changes in the TGS when it is exposed to H_2O and CO, and more work will have to be done to better quantify the effects and to establish the precise chemical changes that occur at the surface. Two possible ways of gaining more insight into the chemical changes would be to try to determine how changing the amount of excess tin affects the conductivity changes, and to determine if there are OH groups present on the surface.

Acknowledgements

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