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SURFACE AND VOLUME EFFECTS OF MOISTURE

Clarkson University

Didier Kane and Henry Domingos

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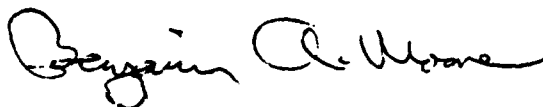Griffiss Air Force Base, NY 13441-5700

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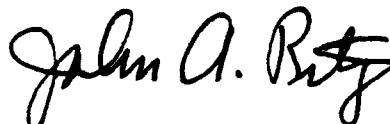RADC-TR-88-153 has been reviewed and is approved for publication.

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This report describes two major types of moisture sensors, surface conductivity sensors and aluminum oxide volume effect sensors. Physical mechanisms are discussed and experimental data presented. It has been found that thermal silicon dioxide is stable during package assembly, but aluminum oxide experiences a structural change at 360°C.

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TABLE OF CONTENTS

i

EVALUATION

The objective of this effort was to research the interaction of water vapor with surface conductivity (SiO_2) and aluminum oxide volume effect moisture sensors. Modes of interaction studied included chemisorption, adsorption, and absorption. Models for the response to moisture for each sensor are presented with the primary mechanism(s) identified in each instance. The dominating interaction of moisture with SiO_2 is physical adsorption while aluminum oxide sensor response is more complex depending on initial absorption of water vapor followed by physical adsorption and then by capillary condensation. The latter process is influenced by the moisture concentration gradient and surface tension resulting in surface curvature which is a function of pore diameter of the aluminum oxide.

The thermal stability of these sensors was studied over a temperature range that a microelectronic device might experience during package sealing operations. Differential Scanning Calorimeter (DSC) measurements of the surface conductivity sensor confirmed existing literature in that no thermal aging effects were observed. However, similar experiments with the aluminum oxide sensor revealed a marked change in structure at around $360^{\circ}C$. This value is different than the value of $250^{\circ}C$ found by other researchers using different techniques (1). Confirmation of this higher transition temperature was made using moisture evolution analysis. The reason for this upward shift in transition temperature could be improved proprietary manufacturing processes. More work is needed in evaluating state-of-the-art aluminum oxide volume effect sensors to confirm this.

The major limiting factor in applying these sensors to microelectronic package ambient in situ moisture monitoring is sealing temperature. The aluminum oxide sensor can only be directly measured (no calibration shift) in low temperature sealed devices such as welded TO type metal cans while the surface conductivity sensor seems amenable to all sealing processes but has not been often used. However, the aluminum oxide sensor has been widely used with success as a moisture screen (2) and as a monitor with either post measurement recalibration or with calibration estimated from the devices in the same manufactured lot (3,4,5). If the observed upward trend in aluminum oxide transition temperature is the result of improved processing, then the potential for a direct reading in a high temperature sealed microelectronic package (i.e. CERDIP at $450^{\circ}C$) is a possibility.

BENJAMIN A.MOORE
Project Engineer

(1)   C. Lin and S.D. Senturia, "Fundamental Studies of the Aging Mechanism in Aluminum Oxide Thin Films", RADC/NBS Workshop on Moisture Measurement and Control for Semiconductor Devices, III, NBSIR 84-2852, Pgs 129-139.

(2)   C.M. Roberts, Jr., "Moisture Content Control Using Alumina Sensor," RADC/NBS Workshop on Moisture Measurement and Control for Semiconductor Devices, III, NBSIR 84-2852, Pgs 162-170.

(3)   H. Joss, "Moisture Sources and Measurement in CERDIP Packages with Alumina Sensors," RADC/NBS Workshop on Moisture Measurement and Control for Semiconductor Devices, III, NBSIR 84-2852, pgs 153-161.

CHEMISORPTION OF MOISTURE ON SILICON DIOXIDE

1) Introduction

The major difference between physical and chemical adsorption lies in the difference in the energy levels that hold a molecule onto a surface; for electrostatic and for Van der Waals types of interaction, the energy levels involved are relatively low, which corresponds to a ''physical'' adsorption; when a chemical bond exists between the adsorbed molecule and the surface on which it is adsorbed, one usually refers to it with the term ''chemical'' adsorption or ''chemisorption''.

2) Chemisorption Model

The chemisorption of water vapor molecules on silicon dioxide is known to be dissociative, and follows the following scheme:

Si----O----Si + H_2O = Si----OH   HO----Si
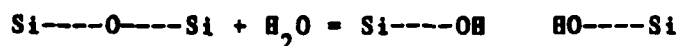
This leads to an activation energy Ea for the adsorption.

In order to simplify the model, let us first assume that the silicon dioxide surface is homogeneous and that the chemisorption is not dissociative.

If n and nt represent respectively the number of atoms that are ''occupied'' (i.e. on which a water vapor molecule is chemically adsorbed) and the total number of atoms on the adsorbate, the adsorption rate at any time t follows the kinetic theory of gas and can be written:

$$\frac{dn}{dt} = \frac{P}{\sqrt{2\pi m k T}} \cdot K \left(1 - \frac{n}{nt}\right) \cdot \exp\left(\frac{-Ea}{RT}\right)$$

where K is an efficiency coefficient.

The desorption rate can be written:

$$-\frac{dn}{dt} = K \cdot \frac{n}{nt} \cdot \exp\left(\frac{-Ed}{RT}\right)$$

At equilibrium, these two rates are equal, which leads to:

$$\frac{n}{nt} = \frac{aP}{1 + aP} \quad \text{with} \quad a = \frac{K}{K} \cdot \frac{\exp\left(\frac{Ed-Ea}{RT}\right)}{\sqrt{2\pi m\, RT}}$$

Let us now take into account the dissociative aspect of the chemisorption. Let us consider a surface made of nt identical atoms surrounded by X neighbors, on which water vapor molecules are dissociated into two identical radicals Si—-OH. The probability for a given atom hit by a water molecule to be ''free'' (unoccupied) is $(1 - n/nt)$. In order for the chemisorption to occur, the water vapor molecule must hit a free atom having a free neighbor.

For evaluating the probability that an atom hit by a molecule be free, we must distinguish between mixed pairs (free atom and occupied neighbor) and free pairs (free atom and free neighbor). As n atoms are occupied, the number of water vapor molecules is $n/2$, the number of occupied pairs is $n/2$ and the number of mixed pairs is $Xn/2$. If $Xnt/2$ is the initial number of free pairs, the number of pairs that can participate to the chemisorption process at any time t is $X(nt-n)/2$.

In addition, $Xnt/2 - n/2$ is the total of the number of mixed pairs and of free pairs, i.e. the total number of pairs in which at least one atom is free. Let $nt/n = Z$; the probability for an atom neighboring a free atom to become a free pair with this atom is given by:

$$\frac{X \left(\dfrac{nt-n}{2} \right)}{\dfrac{Xnt}{2} - \dfrac{n}{2}} = \frac{X(1-Z)}{X-Z}$$

and the desorption rate will be proportional to:

$$Z \cdot \left[1 - \frac{X(1-Z)}{X-Z} \right] = \frac{Z(X-1)}{X-Z}$$

As in the previous case, these two rates are equal at equilibrium, which leads to:

$$Z = \frac{\sqrt{bP}}{1 + \sqrt{bP}} \qquad \text{with } b = a \left(\frac{X}{X-1} \right)$$

Because of the lateral interactions between adsorbed molecules, the activation energies for adsorption and desorption change with the number of chemisorbed molecules, hence with Z. For water vapor on silicon dioxide, the literature indicates that the adsorption energy can vary from 14 to 10

3

Kcal/mole between the beginning and the end of the chemisorption mechanism.

However, regardless of the complexity of the proposed model, the chemisorption will always be limited by the number of available free pairs, which makes chemical adsorption neglectable (on a quantitative point of view) as compared to the physical adsorption that will completely and instantaneously cover the adsorbate.

PHYSICAL ADSORPTION OF MOISTURE ON SILICON DIOXIDE

1) Introduction

The model currently used to describe water vapor adsorption on silicon dioxide (interelectrode material for the surface conductivity moisture sensors) is the ''B.E.T.'' model already described in detail in the final report for the contract F30602-81C-0206 (Chapter 7) entitled ''Non-Destructive Moisture Measurement in Microelectronics'': in this report, the model was applied to the physical adsorption on the cavity walls of the package (Au plated), but the basic equations remain valid for other materials, i.e. for SiO_2. In this chapter, we will therefore use these equations to propose a physical explanation for the effect of moisture on the electrical characteristics of a surface conductivity sensor.

2) Evolution of the leakage current of a surface conductivity sensor between the desorption temperature and the ''Dew-point''.

The electrical response of an interdigited surface conductivity sensor exhibits a slope change between the desorption temperature and the ''dew-point'' (as can be seen on Figure 3 of the above referenced final report reproduced below.) The purpose of this paragraph is to propose a physical model for this observation, based on the interaction mode of water vapor with the SiO_2 during the cooling of the package.
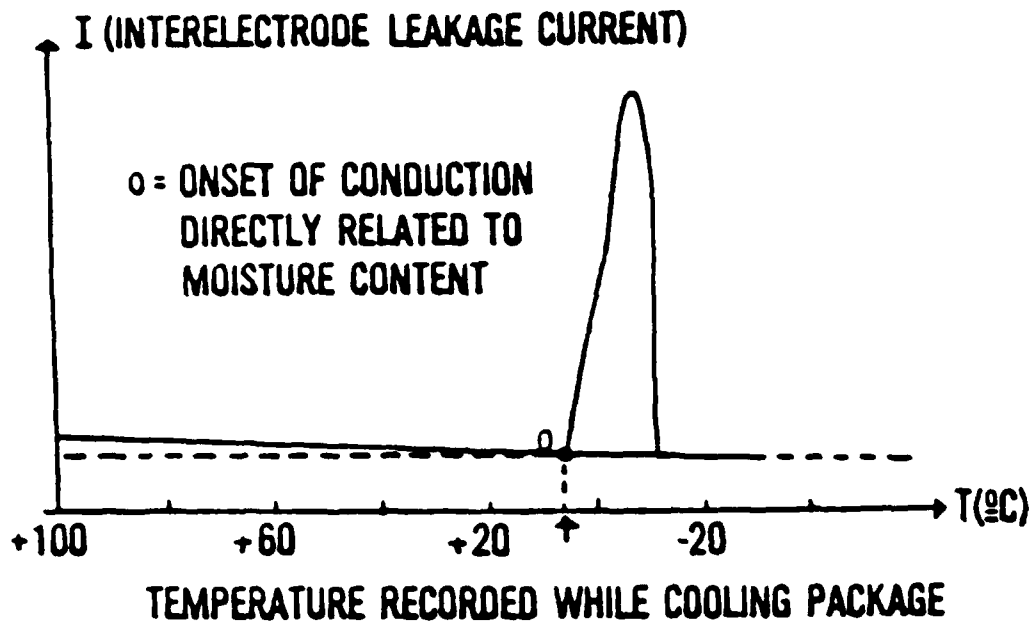
In the temperature range that we are concerned about, water exists in the form of water vapor, whether adsorbed on the sensor, on the package internal surfaces or as an element of the gaseous atmosphere of the cavity. As direct ionic conduction between the electrodes through this gaseous medium is very low, the primary contributor to the measured leakage current is the surface conductivity of the insulating interelectrode medium, namely the silicon dioxide.

It is well known that the surface conductivity of most materials has an activation energy, and SiO_2 is no exception to this rule. The equation that most people use for the surface conductivity (σ) of silicon dioxide in the presence of moisture is:

$$\sigma = K \cdot m \cdot \exp \left(\frac{-EM}{RT} \right)$$

where K is a proportionality factor, Em is the activation energy and m the amount of physically adsorbed water vapor.

ELECTRICAL RESPONSE OF SENSOR

I (INTERELECTRODE LEAKAGE CURRENT)

o = ONSET OF CONDUCTION
DIRECTLY RELATED TO
MOISTURE CONTENT

T(ºC)

+100   +60   +20   -20

TEMPERATURE RECORDED WHILE COOLING PACKAGE

Expected Response Curve for an Hermetically Sealed Package

As previously mentioned, the BET model can be used to quantify the amount (m0) of adsorbed water vapor as a function of the relative humidity (r) and the temperature (T):

$$m = \frac{m0\ c\ r}{(1-r)(1+[c-1]r)} \quad \text{with } c = \exp\left(\frac{E1-E1}{RT}\right)$$

where m0 is the amount of water necessary to cover the SiO_2 with one monolayer, E1 is the heat of adsorption of water vapor and E1 is the heat of evaporation of water vapor.

Having determined the amount of adsorbed water, one now has to take into account the decrease of the activation energy for surface conductivity with the amount of adsorbed moisture, which can be written:

Em = E0 (1-B.m)

where E0 is the activation energy for surface conduction in dry conditions and B is another coefficient of proportionality.

For a given relative humidity, the interelectrode leakage current will therefore be proportional to a function of the type:

$$- A \exp(T) \cdot \exp\left(\frac{B - C\exp T}{T}\right)$$

which is a good approximation of the slope observed over the temperature range of interest.

7

ADSORPTION OF WATER VAPOR ON ALUMINUM OXIDE

The BET model described in the previous paragraph is still valid as a first approximation. However, the water vapor adsorbed on Al_2O_3 has been seen to exhibit a continuum of energy levels (between 15 and 12 Kcal per mole) depending on the proportion of the surface covered by the water vapor. It is currently assumed that the energy holding the molecules of water vapor ontop the aluminum oxide surface decreases with the amount of adsorbed molecules, because of the increasing lateral interactions between the adsorbed molecules. These interactions are minimum in the case of silicon dioxide because of the dissociative aspect of the adsorption.

Higher energy levels have also been reported and are believed to be related to a tendency of the aluminum surface atoms to complete their 3p level through a bond with the hydroxyl group of a water molecule, which can be represented by the following scheme:

```
            H
            |
            0....H
            |
     0--A1--0
            |
            0
```
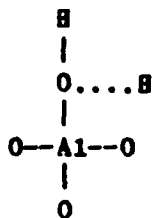
In this configuration. the remaining proton is electrostatically attracted by the oxygen atom that completes the 3p level of the surface aluminum.

ABSORPTION OF MOISTURE BY ALUMINUM OXIDE

The absorption of water vapor by aluminum dioxide is a two-step process. The water vapor molecules first diffuse through the pores of the aluminum oxide and then get adsorbed on their walls.

1) Diffusion:

The concentration gradient between the surrounding atmosphere (i.e. the internal atmosphere of a package cavity) and the pores of the aluminum oxide is at the origin of the diffusion mechanism.

The mechanism of the diffusion of water vapor in a porous aluminum oxide (for instance, an electrolytic Al_2O_3 as the one used in the manufacture of moisture sensors) has been found to be best described by a Fickian model, which can be written:

$$\frac{d(c)}{dt} = \frac{d}{dt} \left(De \frac{d(c)}{dx} \right)$$

where c is the concentration in water vapor molecules (on the surface and in the pores of the aluminum oxide), x is the direction of the pores (that are assumed to be parallel and cylindrical in this simplified model) and t is the time (counted from the beginning of the diffusion mechanism, at which the concentration on the surface is maximum). De is the diffusion constant for water vapor in aluminum oxide.

2) Adsorption on the inner walls of the pores

The above diffusion mechanism is slowed down by the adsorption of some of these water molecules onto the pore walls, which decreases the free path available for the diffusion, and in turn, the diffusion constant. These molecules tend to plug the pores, which modifies the dielectric constant of the porous medium.

This principle is at the origin of the volume effect aluminum oxide moisture sensor which is made of an aluminum electrode deposited on a silicon substrate, and of a porous electrolytic aluminum oxide between the aluminum electrode on top of which a thin layer of porous gold acts as an upper electrode. The complex impedance of the sensor, easily measurable between the two electrodes will be directly proportional to the dielectric constant of the aluminum oxide, hence to the relative humidity to which the sensor is exposed, through the concentration gradient of the water vapor molecules.

The smaller pores will fill up first, then the bigger, until all the pores are plugged, at which time the sensor is saturated. The beginning of this adsorption process is similar to a multilayer BET process (described in a previous chapter), but the end of the filling of the pores can be better described with a capillary condensation model.

In that case, the driving force for the filling of the pores is not only the concentration gradient, but also and mainly the surface tension and the resulting surface curvature, which depend on the diameter of the pores.

THERMAL CHARACTERIZATION OF THE SILICON DIOXIDE
USED IN THE MANUFACTURE OF SURFACE CONDUCTIVITY SENSORS

1. Introduction

The purpose of this section of the program was to evaluate the thermal stability of the materials used in the manufacture of interdigited surface conductivity sensors over a temperature range slightly exceeding the maximum temperature that could be seen by the device during the assembly operation. While no major temperature related aging problem has ever been reported for such sensors, these experimental results are interesting for comparison purpose with other materials.

2. Differential Scanning Analysis (DSC) Characterization:

2.1: Description of the samples

The samples used for this analysis were pieces of wafers processed identically to actual sensors fabrication, up to and including the thermal silicon dioxide growth. The total oxide thickness was 750 nm; the oxide is a multilayer (dry/wet/dry) structure, and $C_2H_3Cl_3$ has been added to the O_2 atmosphere for neutralizing Na and other contaminating alkali metal ions.

2.2: DSC Results

Figure 1 represents a typical DSC plot on our SiO_2 samples; it can be noted that no major transition occurs over a temperature range [+40, +460 C]; regardless of this lack of abrupt variations, the curve will be useful for comparison purpose with Al_2O_3. As can be seen, the curve tends to reach a maximum in the 300 to $400^{\circ}C$ range, which seems to indicate that all the water molecules have been desorbed from the SiO_2 surface. The small exothermal peak at $435.5^{\circ}C$ has not been consistently found on the samples. It can therefore be concluded from this curve that the material is stable over a temperature range that extends beyond the highest temperatures seen by the sensor during the sealing process. No degradation of a surface conductivity sensor due to thermal stress during the assembly operation is to be expected.

Figure 1

DSC

Sample: DK SIO2
Size: 8.4MG
Rate: 20C/MIN
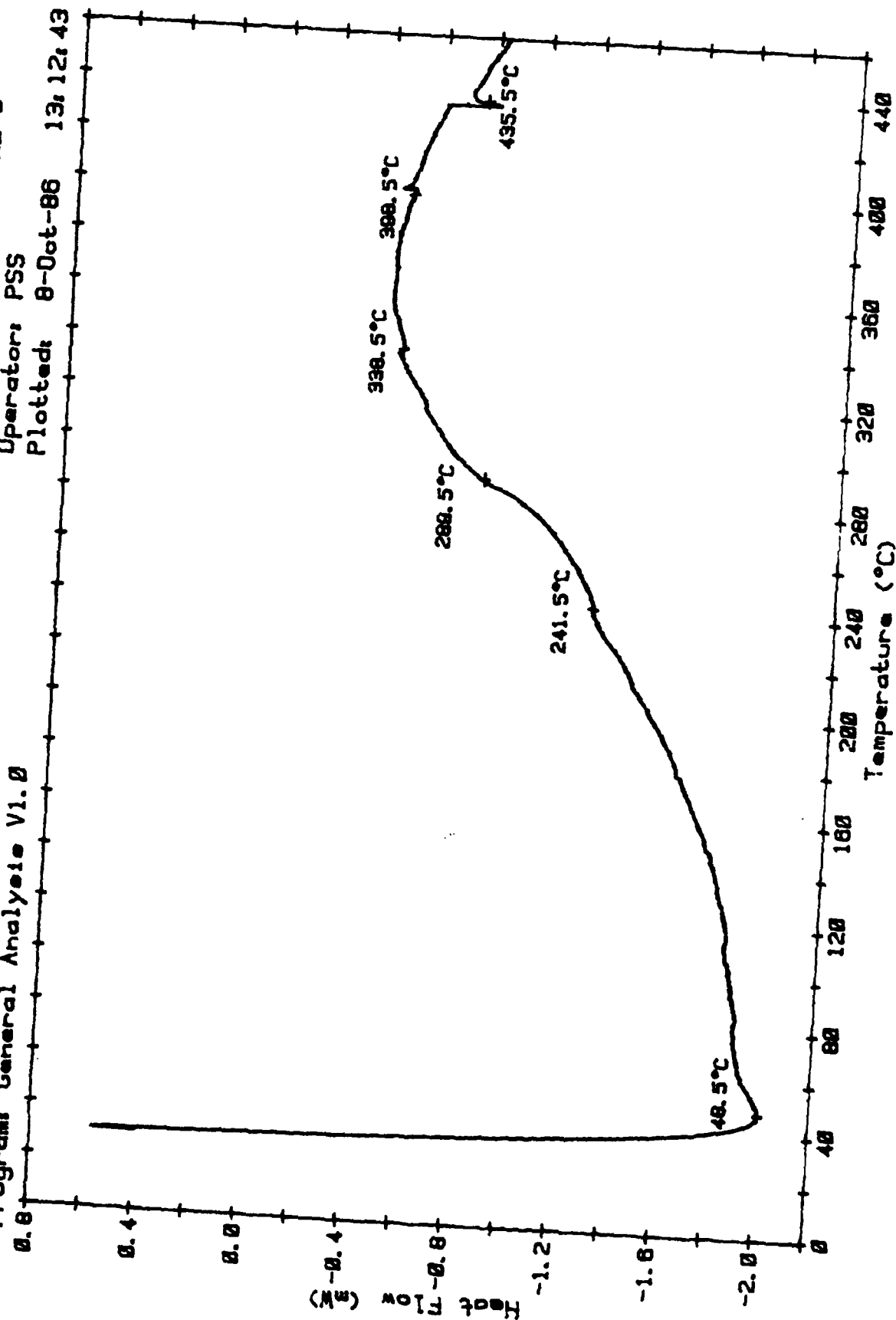Program: General Analysis V1.0

Date: 8-Oct-86   Time: 11:42:37
File: PE480.07 P EVAL 5
Operator: PSS
Plotted: 8-Oct-86   13:12:43

48.5°C
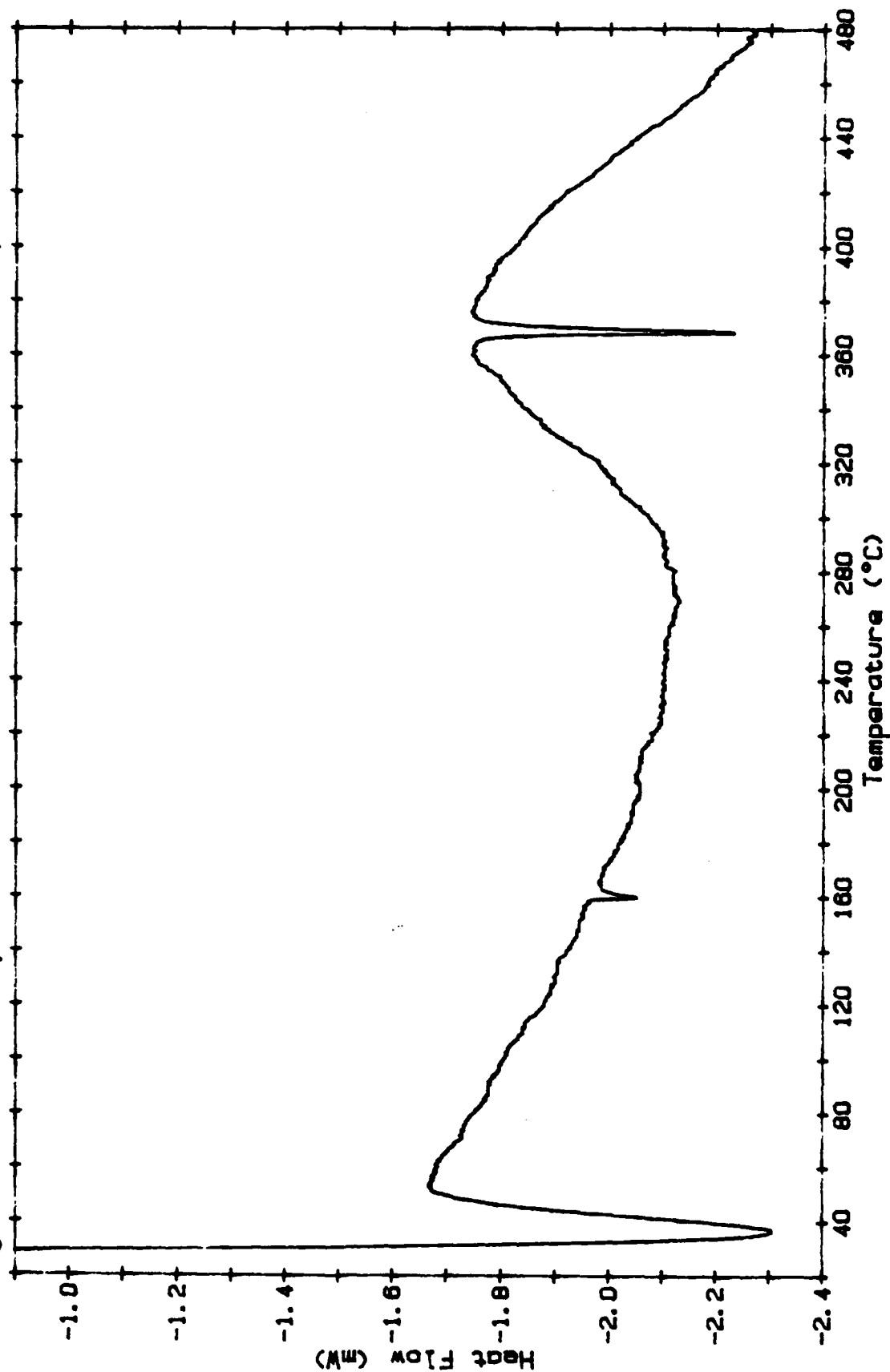
241.5°C

288.5°C

338.5°C

398.5°C

435.5°C

Heat Flow (mW)

0.8   0.4   0.0   -0.4   -0.8   -1.2   -1.6   -2.0

Temperature (°C)

40   80   120   160   200   240   280   320   360   400   440

DuPont 1090

12

Figure 2

DSC

Sample: AL203.1
Size: 13.2MG
Rate: 20 C/MIN
Program: General Analysis V1.0

Data: 29-Dec-86   Time: 9:57:59
File: AL203.01
Operator: DK
Plotted: 29-Dec-86   11:02:55

Heat Flow (mW)

Temperature (°C)

DuPont 109

13

THERMAL CHARACTERIZATION OF THE ALUMINUM OXIDE
USED IN THE MANUFACTURE OF VOLUME EFFECT SENSORS

1. Introduction

An aging mechanism of the volume effect sensors has been reported in the literature, which results in the universally recognized need to recalibrate these devices after any exposure to a high temperature. Infrared spectrum and isotope exchange have been used by Professor Senturia at MIT to point out a change in characteristics at temperatures greater than $250^{\circ}C$, attributed to a gradual change from pseudobohemite to alpha-alumina. Our intent in this program was therefore to try to use DSC to confirm the nature of the above structural changes.

2. DSC Characterization

2.1. Description of the samples

The samples used for this characterization were wafers believed to be processed as identically as possible to actual commercial volume effect surface conductivity sensors. The exact nature of the processing steps remains proprietary information.

2.2. DSC results

Figure 2 is a typical DSC plot on our Al_2O_3 samples. As can be seen, the samples exhibit an exothermal behavior down to $260^{\circ}C$, with a peak at approximately $150^{\circ}C$, and an endothermal behavior over this temperature, with an exothermal peak at $360^{\circ}C$. This does not seem to confirm the change to alpha-alumina around $250^{\circ}C$ found by other researchers with other techniques, but it tends to indicate a gradual transformation starting at this temperature, with a drastic structural change around $360^{\circ}C$. One can therefore conclude that any assembly procedure beyond $360^{\circ}C$ will modify the structure of aluminum oxide moisture sensors (more efforts would be needed to identify the nature of this transformation), which might explain the sensitivity loss of these sensors when exposed to high temperatures.

3) Moisture Evolution Analysis

In order to confirm the existence of a structural change of the aluminum oxide moisture sensors around $360^{\circ}C$, the samples have been tested by moisture evolution analysis (MEA).

TEMPERATURE	BLANK	SAMPLE	ACTUAL MOISTURE
$100^{\circ}C$	16.1	41.0	24.9
$200^{\circ}C$	24.8	58.4	33.6
$300^{\circ}C$	33.5	60.2	26.7
$400^{\circ}C$	19.6	87.1	67.5
$500^{\circ}C$	16.8	99.6	82.8

These results are summarized in Figure 3: As can be seen on Figure 3, there is a change in slope between $300^{\circ}C$ and $400^{\circ}C$, which tends to confirm the existence of a structural change as suspected from the DSC data.
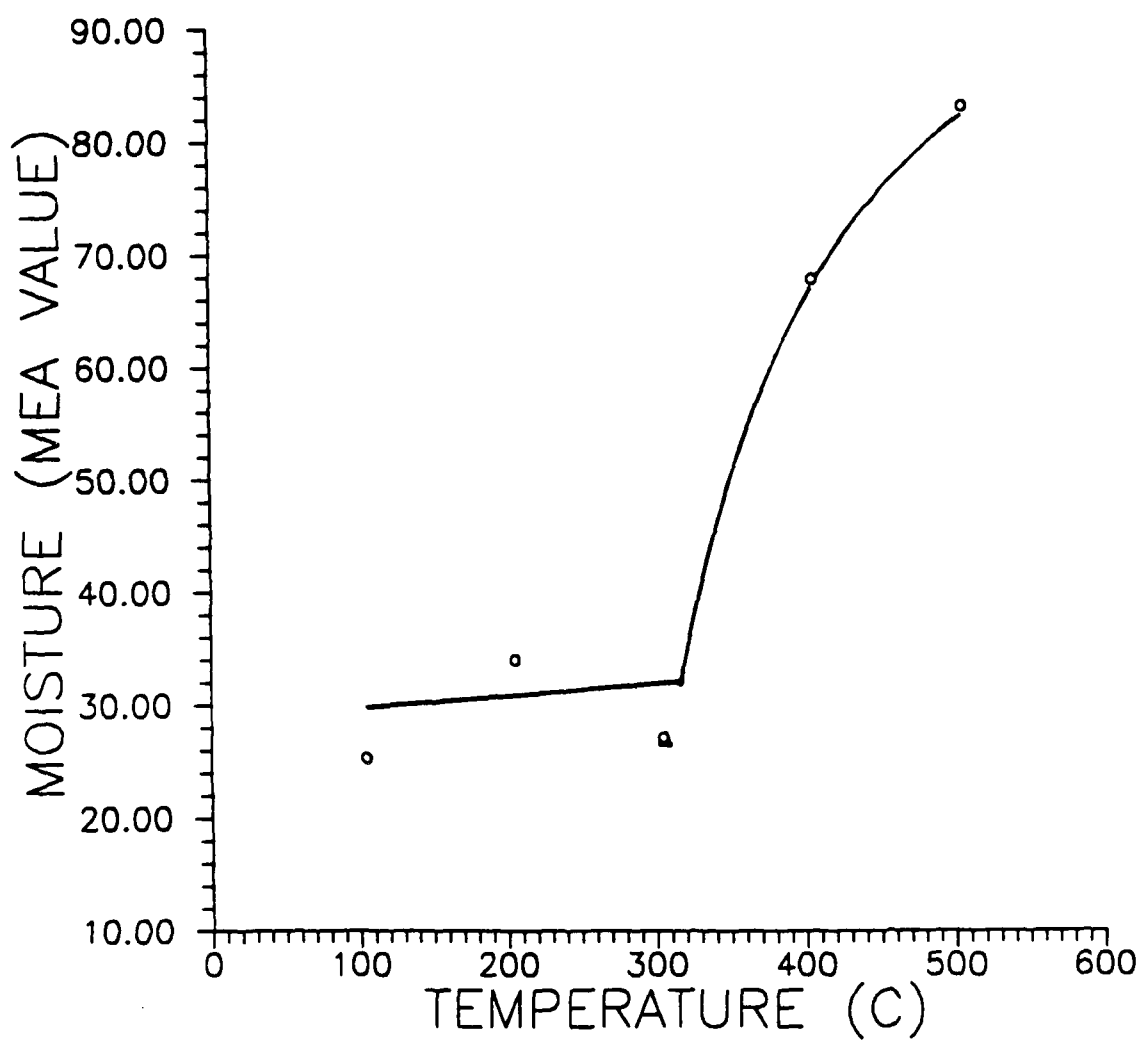
Figure 3

RECOMMENDATIONS FOR THE USE OF MOISTURE SENSORS IN THE MANUFACTURE OF MICROELECTRONIC DEVICES

Based on the thermal characterization of the materials used in the manufacture of moisture sensors for microelectronics, it can be concluded that:

1) SiO_2 surface conductivity sensors should not present any degradation after exposure to package assembly and can therefore be used with no restriction.

2) Al_2O_3 volume effect sensors exhibit a structural change that affects their ability to absorb moisture when exposed to temperatures higher than $360^{\circ}C$. It is therefore recommended to either avoid any assembly temperature higher than this threshold or calibrate them after assembly (provided that the sensitivity range on the calibration curve remains satisfactory).

CONCLUSION

The work presented in this report gives an understanding of the interaction modes between moisture and the materials used in the manufacture of the major commercially available moisture sensors for microelectronics. Chemisorption, physical adsorption and absorption of water vapor on silicon oxide and aluminum oxide have been studied on a theoretical basis. A thermal characterization of these materials by Differential Scanning Analysis (DSC) and Moisture Evolution Analysis (MEA) has been done to assess the limits of their applicability for moisture measurement in microelectronic packages. It has been determined that thermal silicon dioxide is stable during package assembly while aluminum oxide exhibits a structural change at 360°C, which can affect the sensitivity of the volume effect sensors when exposed to higher temperatures.

Keywords: surface conductivity sensor, aluminum oxide sensors; (KT)

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