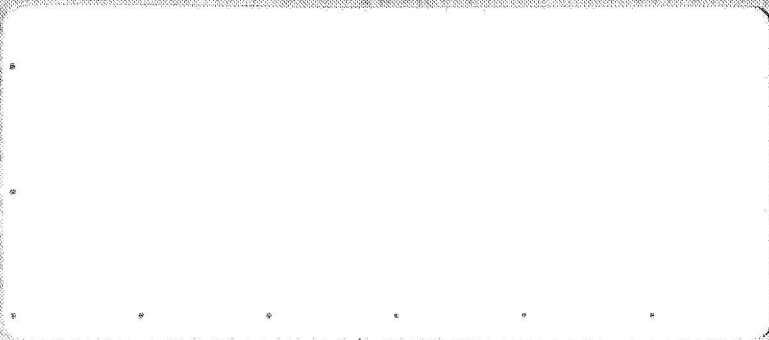


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QUARTERLY STATUS REPORT #2
SILICON SURFACE PASSIVATION FOR DEVICES
NASA RESEARCH GRANT
NGR 36-003-067

School of Engineering
Case Western Reserve University
Cleveland, Ohio

Prof. Alan B. Kuper, Principal Investigator

National Aeronautics & Space Administration
Electronics Research Center
Cambridge, Mass.

F. J. Cocca, Grant Monitor

March 1, 1969

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I. Research Completed

Oxide Water Contamination

In this quarter this research was completed. Principal effort was in analysis of our previously reported diffusion data, and interpretation of interaction between Na and water which was measured last quarter. Following is a concise report of results and conclusions to be published in the Extended Abstracts, Electronics-Semiconductors, Electrochemical Society Meeting, May, 1969.

WATER CONTAMINATION IN THERMAL OXIDE ON SILICON
G. L. Holmberg and A. B. Kuper
Case Western Reserve University
Cleveland, Ohio

Water contamination in thermal oxide on Si is of interest in connection with device process control and reliability. Water-related species, such as OH, have been found to be present in thermal oxide on Si¹. Also, hydration is known to annihilate fast interface states². Water may also affect oxide properties and interact with charged impurities. In the present work, radioactive water has been used to controllably hydrate conventional thermal oxide under conditions approximating device operation.

Oxides were wet-grown at 1200°C to 5400 Å on 10 ohm-cm n-type Si wafers and baked in dry nitrogen for 30 min. at 1000°C. Samples were hydrated with tritiated water vapor (250 mC/gm specific activity) in an evacuated cell at controlled temperature, pressure, and time. Temperatures ranged from 50° to 250°C, times from 15 min. to 8 hrs., and water vapor pressures from 25 to 400 mm Hg (partial pressure of 25 mm of water vapor in air corresponds to relative humidity of approximately 70% at 90°F). MOS electrical measurements were made using evaporated Al dots and back contact. Hydrogen profiles were obtained by dilute HF etch-sectioning of oxide and liquid scintillation counting

of etchant.

Fig. 1 shows development of profiles with time (some curves represent several samples). Diffusion length after one hour may be seen to be roughly 5000 Å which gives $D(200^{\circ}\text{C})$ more than an order larger than D extrapolated from available higher temperature data for fused silica³.

Variation of the diffusion temperature gave a set of profiles similar to those in Fig. 1. Estimated diffusion activation energy was 0.3 ev. Pressure variation for four-hour hydrations at 200°C gave a set of profiles similar to the four-hour profile in Fig. 1. Increased pressure gave the profile a nearly parallel upward shift with a $P^{1/2}$ dependence.

Hydrogen measured at concentrations as high as $5 \times 10^{18}/\text{cc}$ at the Si interface did not annihilate interface states or appreciably shift flat-band voltage. (Hydration at 800°C annihilated all interface states, as expected).

Fast penetration, nearly exponential bulk profiles, and low activation energy suggest diffusion of water species at these low temperatures may be via micropores⁴. In this model the near-surface layer is assumed to be heavily micropored, giving the observed spike. Further evidence for this may be that surface concentration (Fig. 1) increased with time although water pressure in the system was constant. An outdiffusion experiment (Fig. 2) showed that segregation of water species was characteristic of the surface layer after outdiffusion, even with initial etching. Outdiffusion rate was comparable to indiffusion rate, therefore much faster than reported values for outdiffusion of tritiated-steam-grown oxides⁵.

In another set of experiments (Fig. 3), both radiotracer Na^{22}Cl and tritiated water were diffused. In oxides contaminated with about 10^{17} Na/cc as shown, a 200°C hydration diffused about an order of magnitude more hydrogen than did an identical hydration of samples containing only residual Na ($\approx 10^{16}/\text{cc}$). Hydration gave no change in flat-band voltage (V_{fb}) set by the Na. Sodium at

600°C was found to diffuse faster, as reported⁶, and to give a larger shift of V_{fb} in a wet than in a dry diffusion.

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T. E. Burgess and F. M. Fowkes, J. Electrochem. Soc. 113, 63C (1965).
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II. Current Program Plan

Approach and Emphasis

This report describes plans for remainder of grant period. We proposed to extend our approach to other aspects of the SiO_2/Si system in addition to those we had been studying. We proposed to make use of lowered-temperature pre-screening to identify anomalies and to try to develop simple, useful tests.

Four new research areas were proposed. In consultation with the Grant Monitor, after studying failure mode reports which he has supplied to us, we have concluded that the most fruitful among the four to attack first is the area of outer surface failure. This refers to failures due to charge, such as surface-ions, on thin oxide, and due to oxide which is locally permeable. Reasons for this choice are:

- (1) Failures in Si IC's are attributed to this.
- (2) The surface-charge effect has been demonstrated.
- (3) More quantitative information is needed.

In what follows by "surface" is meant outer surface of oxide.

Specific Approach

Program consists of three main parts:

- (1) Combine electrical/chemical method to study surface impurities.

- (2) Develop specific lowered temperature test for surface ions.
- (3) Study oxide local fine-structure.

Details of Program

In area (1) above, goals are:

- (A) Identify sources and types of surface charge.
- (B) Quantitative measurement of surface ion parameters: concentration, charge concentration, mobility. Also dependence on oxide surface and ambient parameters.

Specific device processing and encapsulation determine impurities responsible for surface failure. Any method of identifying these impurities must be specific to surface impurities and measure in-situ, system nearly unperturbed.

The procedure planned for conduction impurity identification is to measure reaction products from the electrolysis. A ring-dot geometry will be used on oxide which should make quantitative interpretation possible. We plan to monitor current and do impurity analysis in situ.

Analysis of Gaseous Reaction Products

Surface current gaseous products from electrolysis will be measured with a gas analyzer for quantitative analysis.

Assuming a minimum current of 10^{-12} A

$$N = \frac{Q}{q} = \frac{It}{q} = \frac{10^{-12} t}{1.6 \times 10^{-19}} = 6 \times 10^6 t \text{ charges}$$

Sensitivity of the Ultec Quad 150A Residual Gas Analyzer is approximately 10^7 molecules, which should be satisfactory. The instrument,

which is available for use on this project, is capable of identifying unknown species from hydrogen to mass 300. For example, chlorine is 70, acetone about 45. Characteristic spectra are available for aid in identification.

The problem with this measurement is that conduction will occur in our cell at near atmospheric water-vapor pressures, while the analyzer does not operate at pressure above 10^{-6} mm. We plan to solve this in one of two ways: either (1) use a controlled leak to drop pressure, or (2) freeze out the water. The first method sacrifices sensitivity but allows a continuous measurement during electrolysis. This method will be used for relatively large amounts of gas. Second method is a measurement of total evolved gas and has the disadvantage that components with low vapor pressure will be missed. Warm-up may reveal these species however.

Analysis of Solid Reaction Products

The ring-dot structure will be used to concentrate impurity by making the dot small and plating to it. If sufficient impurity can be concentrated, analysis will be possible with the microprobe. Activation analysis, more difficult, may be necessary.

Estimate of Surface Current-Voltage

For a ring-dot structure with radii a, b , resistance R is:

$$R = R_s \frac{1}{2\pi} \ln \frac{b}{a}$$

where R_s is sheet resistance

$$R \doteq \frac{1}{6} R_s$$

for $\frac{b}{a} \sim 3$.

Sheet resistance of clean fused quartz varies from about 10^{15} ohms in 0 R. H. to $10^{11} - 10^{13}$ ohms in 70% R. H. Thus to measure 10^{-12} A,

$$V = 10^{-12} \frac{(10^{15} - 10^{11})}{6} = 170 - 0.02 \text{ v.}$$

which poses no special problem.

Mapping

Once we have identified the mobile species, we will use the ring-dot on oxide to simulate device charge-flow under controlled humidity. We are interested in "mapping" the surface to determine uniformity of surface impurity flow. Also we want a quantitative measure of transport number, sign, and mobility. We propose to do this by comparing integrated surface current with autoradiographs using radiotracer impurities such as Na. If mapping shows uniform drift of tracer, then in simplest form,

$$Q = \int j t = q \int_0^w \frac{x}{w} N(x) dx.$$

Determination of $N(x)$, impurity distribution along the field direction, by densitometer and calibration, will enable analysis of surface ion flow mechanism.

Mapping may be able to reveal whether ion flow is localized or patchy, especially at low humidity.

Estimate of Autoradiography

We assume that about 10^{11} impurities/cm² are distributed singly-charged over the oxide. This is the minimum required to invert the underlying Si in the Philco experiments.

Number of disintegrations/sec.

$$- \frac{dn}{dt} \cong \frac{n_0}{\tau} (1/2)^{\frac{t}{\tau}}$$

where τ = half-life. Thus for a carrier-free radioisotope with 10 hr. half-life, initial total disintegration rate is approximately

$$- \left(\frac{dn}{dt}\right)_0 = 3 \times 10^6 / \text{sec} - \text{cm}^2$$

Sensitivity of film for beta particles is such that $10^7 / \text{cm}^2$ is required for grainy films (9u), up to 10^9 for fine-grained films (2u), in order to produce a density 0.6 above background. Thus, seconds to hours exposure is estimated to be required, trading off choice of half-life, specific activity, and resolution.

(2) Lowered temperature test for surface ions.

A pre-screening test for surface ions must separate their contribution from that of others. For example, in a reverse-biased diode, excess current might be due to high surface recombination, channel, microplasmas, junction edge shunts, as well as surface ions.

The surface conductivity of glass is strongly influenced by adsorbed water film. Thus it would seem that, although impurity species and surface condition may vary, characteristics of the water film may be relatively constant parameters.

It is planned therefore to explore surface conductance in the temperature range around 0°C . If the test-structure shows the expected effect of freezing the water-layer even at low humidity, this will be the basis for developing a diode test.

A diode test of this kind could be quite versatile and sensitive since ion distributions could be "frozen-in" at different biases.

(3) Oxide local fine-structure.

Evidence exists that thermal SiO_2 has local fine structure. As an example, a passivating oxide may be grown to thicknesses of $\approx 1000 \text{ \AA}$ with reasonable yield, but yield is low if oxide is grown to greater thickness and then etched back.

Understanding and minimizing such structure may be important in micro-circuit reliability for passivation against impurity, for integrity in the presence of metal overlayers, and for preventing local breakdown.

Decoration methods, like those used successfully in Ge and Si, will be investigated.

Penetration technique is also planned.

III. Research in Progress

Oxide Surface Conduction

The gas analysis experiment has been designed to identify surface ions. Work is proceeding on developing the electrolysis cell for the gas analyzer. A high-vacuum flange and glass-metal seal have been obtained, the cell has been designed, and is on order with the glassblower.

Preliminary tests were made on current-voltage characteristics of glass surfaces similar to the surface we will be using. Using an available Keithley electrometer, tests were made to determine signal/noise versus humidity in a loosely-closed, shielded chamber. Results were promising and quantitative data is being obtained. For a test vehicle we used a T0-28 type header with approximately .020" path-length over the glass feed-through surfaces.

Interface States

Mr. Caban-Zeda is continuing his graduate thesis work on interface states, principally relaxation of deep-depletion capacitance at 77°K.

On February 7 Dr. Kuper visited with F. Cocca, the grant monitor, M. Liimatainen and other interested personnel at ERC. Dr. Kuper summarized his review of the literature of oxide surface charge flow and of associated failure data. Main discussion concerned specific research approaches proposed to be used.

Personnel

Mr. Thomas O'Mara, who has been technician in the Solid-State Technology Laboratory for two years, will assist in the program 80% of his time, starting March 1. Professor W. H. Ko will allot 10% of his time to the program.

During February, G. L. Holmberg and C. J. Slabinski completed their requirements for the PhD. and left the program.