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Effect of Growth Conditions on the Properties of Thermal Oxides

by P. V. Gray and D. M. Brown

Abstract of Talk to be given at the
Silicon Interface Specialists Conference
November 14 and 15, 1965
Las Vegas

The properties of thermally grown SiO_2 on Si substrates have been studied. Oxidation was performed in an oxygen atmosphere containing varying concentrations of water vapor. It was found that the characteristic stored positive charge in the oxide, the number of interface states and the oxide growth rate vary systematically with water vapor content. In particular, there exists a critical water vapor content in the oxygen above which the growth rate steadily increases. Below this value, the growth rate is nearly independent of water vapor content, and the characteristics of the Si-SiO_2 interface are markedly changed. Most striking is the large number of interface states characteristic of "dry" oxides. The implications of these characteristics in terms of oxide growth kinetics will be discussed. All of this information was obtained from interpretation of the capacitance vs. bias characteristics of Si-SiO_2 (MOS) capacitors grown on (111), (110) and (100) orientated substrates.

Influence of Surface Barriers on PME and PC-Effects after Various Surface Treatments in p-Type Silicon.

by Herbert Mette

U.S. Army Electronics Command, Fort Monmouth, New Jersey)

Measurements of "true" surface recombination velocities, S, indepen of the method of carrier generation, become frustrating and the results inaccura when space-charges are involved. Evidence is given that sufficient barrier heigh exist in p-type silicon after the following surface treatments: (a) one minute etching in CP_4, (b) four minutes boiling in 10 % KOH solution, (c) ten minutes etching at room temperature in HF, (d) five minutes etching at 40°C in one per cent $K_2Cr_2O_7$ solution, to affect seriously such common photoelectric methods for determining S as the steady state photoconductivity method, the photoelectric decay method, and the PME/PC ratio method. Both the photoconductivity and the photomagnetoelectric (PME) open circuit voltage have been measured at room tempe rature for thin p-type silicon samples subjected to the above surface treatments The effects were found to increase linearly with the magnetic field up to 20 kG, but for all surface treatments showed sublinear behavior with photon flux even at relatively low light intensities. The highest PME and PC effects were obtained fo surfaces etched with CP_4; the other surface treatments produced qualitatively identical dependence of the effect with photon flux: A fairly linear increase of the effects occur at wavelengths near the absorption edge, but toward shallow absorption the curves become situated increasingly above the longer wavelength curve and assume a more and more sublinear shape. This effect could be attributed to an accumulation layer in the space-charge region of the crystal. In the region of linear dependencies near the absorption edge, our PME and PC data could be use for calculating an "effective" surface recombination velocity, S*, at the border between the space-charge region and the bulk crystal.

IONIC CONDUCTION IN SINGLE OXIDE GLASSES

M. E. Milberg

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan

It has been generally accepted that, in alkali silicate and borate glasses, electrical current is carried by the alkali ions. The conductivity follows a simple Arrhenius type expression, as might be expected with a single species of current carrier. However, the details of the conduction mechanism are not understood.

Scattered reports in the published literature indicate that, with both Li_2O-SiO_2 and Na_2O-SiO_2 glasses, the conduction activation energy variation with alkali content can be expressed as two straight lines. The junction of the lines varies in these reports from about 15 mole percent alkali oxide to about 35 mole percent, with 33 mole percent a popular figure. These results have been variously interpreted as resulting from compound formation and phase separation in the glasses. Although a break in a property in this composition range is reminiscent of the so-called boron oxide anomaly in alkali borate glasses, the change in boron-oxygen coordination responsible for the latter is very unlikely to have an analogue in silicate glasses.

Recent careful studies in this laboratory have shown that all the alkali silicate glasses, from Li_2O-SiO_2 to Cs_2O-SiO_2, have the same composition dependence of activation energy for conduction. In each case, the plot of activation energy *vs.* mole percent alkali oxide consists of two straight lines of different slopes meeting at about 25 mole percent alkali oxide and an activation energy of about

Anomalous Effect of Voltage Baking on the Inversion Layer Conductivity of MOS Devices

M. Ono: Musashi Works of Hitachi, Ltd., Tokyo, Japan

Abstract: Effect of voltage baking on the inversion layer conductivity of silicon coated with thermally grown oxide has been studied. N channel depletion MOS capacitors fabricated in p-type silicon are used as investigation tools. The Inversion layer conductivity is measured by the source to drain conductivity Gc at zero gate bias.

Effect of baking at 350°C with positive gate bias is that in spite of monotonic increase with baking time of the total surface charge density Nt, corresponding conductivity does not vary proportionally, but rather decreases after initial increase which tends to a maximum.

It is also investigated whether the following baking with negative gate bias can eliminate the effect caused by the previous baking with positive gate bias. For the unit heat treated with positive bias for a short time, reversible change is observed and conductivity tends to the original value monotonically. For the unit received a prolonged heat treatment with positive gate bias, anomalous mode of recovery of conductivity as well as of Nt is observed, i.e. conductivity decreases towards zero overshooting the original value with successive heat treatment with negative gate bias, and further treatment causes the conductivity tend to increase again towards the original value.

In accordance with the anomalous conductivity change, the total surface charge density also shows the anomalous change, i.e. while for the unit heat treated with positive gate bias for a short time, the effect caused can be eliminated reversibly by following heat treatment with negative gate bias, for a unit received a prolonged heat treatment with positive gate bias, Nt decreases, overshoots the original value, changes the sign and then begins to increse towards the original value. When the unit has the opposite sign of Nt, its performance as MOS transistor is that of induced channel type.

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ELECTRON MOBILITY ON SILICON SURFACES

by

Alan Fowler

IBM Watson Research Center
Yorktown Heights, New York

In addition to extended measurements of electron mobility variations on (111) surfaces of silicon reported earlier, measurements have been made on (100) surfaces. At room temperature the variation of mobility with gate voltage and carrier density is similar to that on (111) surfaces, but the (100) surfaces exhibit somewhat (10-25%) higher mobilities. The Hall ratio is also higher. At 77°K and 90°K mobilities as high as 5000 cm^2/V sec have been observed in 100 ohm-cm silicon and as high as 3000 cm^2/V sec in 12 ohm-cm silicon. All samples studied at 77°K exhibited minima in the mobilities in a manner similar to those reported by Fang in gallium doped-oxide samples at room temperature on (111) surfaces. The high field maxima grow as the temperature is lowered. The low field maxima

increase as the temperature is lowered to 90°K but then decrease At 4.2°K there is no evidence of the low field maxima. Neither conventional surface scattering theories nor the models proposed for gallium doped oxides explain this phenomenon.

THE EFFECTS OF ORIENTATION AND ANNEALING ON THE SURFACE CHARGE OF THERMALLY OXIDIZED SILICON

P. Balk

IBM Watson Research Center
Yorktown Heights, New York

ABSTRACT: The rate of thermal oxidation of silicon is a function of the orientation of the exposed crystal face, and can be expressed in terms of a mixed linear-parabolic rate law. The fact that it is the linear part of the reaction (which is probably surface limited) that exhibits the orientation dependence, makes it likely that the electrical interfacial properties also show such dependence. We found from MOS measurements with evaporated Al electrodes that indeed both for dry O_2 and for steam oxidation the surface charge depends on orientation and decreases in the order (111), (110), (100). This relationship is maintained upon P_2O_5 doping of the oxide. Considerable further reduction of the built-in charge is obtained upon annealing of the Al covered surface. This effect is dependent on temperature and duration of the procedure. In addition, it is markedly affected by exposure of the surface to water vapor before evaporation of the Al film. Some typical low values of built-in charge for the (111), (110) and (100) surfaces are 2×10^{11},

1 x 10^{11} and 0.5 x 10^{11} electron charges cm^{-2} respectively. In the annealing process, field effect mobility values as high as the bulk mobility value were obtained both on (111) and on (100) surfaces. The stability of the oxide was found to be independent of orientation.

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October 19[illegible]

[illegible]. J. T. Nelson
[illegible]airman, Technical Program Committee
[illegible].L.
[illegible]ne Laboratories
[illegible], New Jersey

[illegible]:

[illegible] new program [illegible] should shed some additional light [illegible] nature of the Si-SiO2 interface by approaching the fabrication [illegible] a somewhat novel approach. An MOS-Silicon device will be [illegible] by phosphorus ion implantation through a passivating oxide. It will be possible to atomically clean the silicon surface by ion [illegible], deposit silicon dioxide by electron beam techniques and implant the channel through the oxide, all at pressures of less 10^{-7} [illegible]. Contamination from unwanted impurities will be eliminated by backfilling with inert gases and using spectrographic control of the ion source.

The results of this fabrication technique will be evaluated by pulse field effect measurements, C-V plots, and channel conductivity vs temperature measurements.

It should also give a quantitative value for the impact damage of the ion beam by measuring the various quantities before and after annealing.

[illegible] Government supported work, I shall be open to comments or suggestions on how this fabrication technique might be even more effectively utilized to answer current questions regarding the Si-SiO2 interface.

Sincerely yours,

[signature]

ROBERT W. THOMAS
NAVAL AIR DEVELOPMENT CENTER

D. S. Duncan and H. Lawson

Sperry Semiconductor
Norwalk Connecticut
06852

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SURFACE STATE DENSITY
SOME CORRELATIONS WITH SILICON OXIDATION AND DIFFUSION PROCESSES AND DEVICE PARAMETERS

10/11

Surface potential as a function of surface state density can be monitored during device fabrication on properly designed test patterns interspersed with devices to be fabricated.

Such work has led towards a better knowledge of the surface variation due to the various process steps necessary in device fabrication and some of the factors responsible for oxide "charging".

Gold was found to produce large p-type shifts, exhibiting drastic instability with temperature bias treatments.

We have attempted to relate p-n-p device parameters with shifts in the base surface potential for an epitaxial base transistor. Such parameters as I_{EBO} and I_{CBO} show strong dependencies as would be expected. The large variations in current gain obtained with certain heat treatments, however, are more difficult to explain in terms of a shift in the base surface potential alone.

Kinetics of Thermal Growth of Silicon Dioxide Films in Water Vapor and in Water Vapor-Oxygen Mixtures

Takashi Nakayama and F. C. Collins

Department of Chemistry
Polytechnic Institute of Brooklyn

ABSTRACT

The kinetics of growth of silicon dioxide films in mixtures of water vapor, oxygen, and argon have been studied in the temperature range from 859 to 1217°C and in the range of water vapor pressures from zero to 355 torr. and of oxygen partial pressures from zero to 200 torr. The parabolic law is well adhered to in the later stages of growth at all temperatures investigated although the usual non-parabolic region is found for the initial stages at temperatures below 1000°C.

The activation energy for the thermal growth reaction in the presence of water alone is 1.41 eV in the region below 1030°C and 0.77 eV above this temperature. A transition in activation energy to a lower value at higher temperatures is an unusual occurrence. In the present instance it is tentatively attributed to a change in the local structure of the glassy oxide film.

At the lower water vapor pressures, in the absence of added oxygen, the parabolic growth constant has first order dependence on the water vapor pressure but saturation effects are evidenced by strong negative deviations from the first order law at the higher water vapor pressures. The tendency toward lower order kinetics at the higher water vapor pressures is explained by the equilibrium between the water vapor and adsorbed water on the surface of the film. The deviation in the kinetics of growth is in quantitative agreement with the predictions of the Langmuir adsorption isotherm. The data enable the calculation of the adsorption equilibrium constant, as a function of temperature, and the enthalpy of adsorption. The latter accounts for an apparent change in the enthalpy of the diffusion controlled growth process at higher water vapor pressures.

The kinetics of growth in the presence of both water vapor and oxygen are quite complicated. The effect of added oxygen decreases with increasing water vapor pressure and makes zero contribution to growth at

water vapor pressures above 50 torr. in the range of oxygen pressures investigated. The results are interpreted in terms of the displacement of adsorbed oxygen by adsorbed water on the surface of the film.

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GENERAL RELATIONSHIP FOR THE THERMAL OXIDATION OF SILICON

Bruce E. Deal

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Palo Alto, California

ABSTRACT

The thermal oxidation kinetics of silicon are examined in detail. Based on a simple model of oxidation which takes into account the reactions occurring at the two boundaries of the oxide layer as well as the diffusion process, the general relationship $x_o^2 + Ax_o = B(t + \tau)$ is derived. This relationship is shown to be in excellent agreement with oxidation data obtained over a wide range of temperature (700°-1300°C), partial pressure (0.1-1.0 atmosphere) and oxide thickness (300-20,000 Å) for both oxygen and water oxidants. The parameters A, B and τ are shown to be related to the physico-chemical constants of the oxidation reaction in the predicted manner. Such detailed analysis also leads to further information regarding the nature of the transported species as well as space charge effects on the initial phase of oxidation.

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Photoemission of Electrons From Silicon and Gold into Silicon Dioxide

Alvin M. Goodman
RCA Laboratories
Princeton, N. J.

Photoemission of electrons from both silicon and gold into thermally grown silicon dioxide layers has been observed. In each case the energy threshold for photoemission is found to vary with the electric field in the oxide. Within experimental error this variation is consistent with the theoretical Schottky effect assuming an effective value of image force relative dielectric constant of about 2.15. The extrapolated zero field threshold energies for silicon and gold are about 4.2eV and 3.8eV respectively. From measurements of the photocurrent versus electric field in the oxide it is inferred that the product of the electron mobility in the oxide and the mean time before trapping is of the order of 10^{-13} m^2/V.

October 8, 1969.

Dr. J.T. Nelson, Chairman
Technical Program Committee
I.E.S.C.
Bell Telephone Laboratories
Murray Hill, New Jersey.

Dear Dr. Nelson:

Your October 11 deadline concerning an abstract on original findings in the Mos area puts us in a slight embarrassing position. Our work has not progressed as rapidly as we had expected. One reason for this is that our whole R&D activity has been in the process of physical relocation and about one month of experimental work has been lost. Thus, at this time, even though we have accumulated certain results, they are still not sufficiently conclusive and we hesitate at this time to commit ourselves to a formal presentation. We hope that by mid November we might be in a position to speak informally about our findings.

We would like to make a brief comment about our work on Mos effects. We have constructed a semi-automatic, programmable instrument system capable of collecting transient data under temperature-bias treatment (TBT). The following curves can be readily plotted in rapid succession.

(a) $(CV)_{\pm}(t)$

(b) $(CT)_{V(t)}$

(c) $(Ct)_{V,T}$

Similar plots can be made where C is replaced by I or G. In the $(Ct)_{V,T}$ curves we have observed anomalous characteristics, unfortunately, as mentioned earlier, insufficient data has been accumulated at this time to allow conclusive interpretation. We trust that our inability to submit an original abstract at this time does not preclude our attendance at the meeting.

Cont'd on page 2 .....

Also, recent developments make it highly probable that I cannot attend the meeting. In my stead I would like one of my senior people, a M.A. Clayton, who is actually conducting the Mos investigations, to attend the meeting.

Yours very truly,

W.A. Pieczonka, Project Director
Molecular Electronics.

WAP/ps

SPRAGUE ELECTRIC COMPANY
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AREA 413 - TEL 663-4411

October 7, 1965

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10/11

Dr. J. T. Nelson
Chairman, Technical Program Committee
S. I. S. C.
Bell Telephone Laboratories
Murray Hill, New Jersey

Dear Dr. Nelson:

I could contribute new data on the following subjects for the S.I.S.C. Conference:

1. Surface Leakage on SiO_2

The work presented by me at Princeton has been extended since then in the following respects:

(a) Prove that the surface leakage resistance (R_s) does not depend on voltage.

(b) More detailed dependence of R_s on humidity.

(c) Dependence of R_s on oxide preparation.

(d) Analysis of charging and discharging curves to include bulk leakage resistance.

(e) A discrepancy between theoretical model and observations, consisting in an additional discharge current which depends on polarity, on the (p or n) character of the substrate and on the electrode material. (This work was carried out in cooperation with P. Ho and L. Fedotowsky.)

2. Charge Motion in Insulators

I would like to present an analysis of charge motion in insulators which I found fruitful on Ta_2O_5 and Al_2O_3 insulators. Briefly the results of this analysis are consistent

with charge motion being due to the same ions which participate in the well known anodic growth of these oxides. The application of such an analysis to SiO_2-films will be discussed and some results on one type of oxide preparation which shows particularly large effects will be given. (Most of the experimental results used were supplied by Dr. Dreiner.)

3. Analysis of MOS Impedance

Early analysis has assumed only charges in surface states with no charge in the oxide. Since then presence of charges in the oxide has been found by many authors. I like to comment on the analysis of MOS Impedance curves to distinguish between charges in surface states and charges in the oxide. In particular, I like to discuss the analysis of a distributed energy spectrum of surface states.

Sincerely yours,

Kurt Lehovec

KL/jar

(13)

ABSTRACT

Separation of the Linear and Parabolic Terms in the Thermal Oxidation of Silicon

by
W. A. Pliskin
IBM Systems Development Division

Using accurate film thickness measurements, it was found possible to separate linear and parabolic terms in the thermal oxidation of silicon, and thus obtain much more precise expressions for the thermal oxidation under different conditions. The combined linear - parabolic relation was found to be applicable to various crystallographic orientations. The pure parabolic constant obtained from this relation was the same for different crystal orientations, but the linear term in the relation was found to be very surface sensitive. By these techniques, more accurate parabolic rate constants can be obtained and the linearity of the log k vs. 1/T plot can be extended to much lower temperatures. The activation energy of the parabolic term for steam oxidation was found to be significantly lower than previously published values. The effect of neglecting the linear term in various methods of computing the parabolic rate will be discussed.

EFFECT OF TEMPERATURE ON TRANSFER CHARACTERISTICS OF INTEGRATED FET NOR CIRCUITS

14

by

E. J. Walker

10/11

IBM Watson Research Center
Yorktown Heights, New York

ABSTRACT: Measurements of the voltage transfer function were made in the temperature range 20-200°C on several n-channel integrated FET NOR circuits. The change in the transfer function with temperature is small up to about 130°C. The main effect observed is a lowering of the output voltage in the "off" state. There is a large degree of compensation of the temperature effects in load and active devices in the "on" state, so that the "on" state voltage is virtually independent of temperature. The drop in the "off" state voltage with increasing T is shown not to be a result of increased reverse junction leakage in the output junction, but is ascribed primarily to the shift with temperature of the active device threshold voltage.

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CHARGE STORAGE IN DIELECTRICS

R. P. Donovan
Research Triangle Institute

Electron irradiation of capacitor like structures consisting of polyethylene terephthalate ("Mylar") films with thin aluminum electrodes results in a trapped charge distribution in the dielectric. The decay of the trapped irradiation electrons has been detected and shown to be consistent with a no-retrapping release model based upon a density of traps that is uniform with respect to energy measured from the conduction band.

Irradiation of this capacitor like structure with a beta source (Promethium 147) results in a spontaneous discharge. The breakdown is attributed to the electric field associated with trapped irradiation electrons and occurs at defects in the polyethylene terephathalate film.

Similar capacitor like structures in which the dielectric is either (1) evaporated from a commercial silicon monoxide source or (2) thermally grown on a polished silicon substrate are currently being examined under similar irradiations. Preliminary results indicate that the trap density of both types of silicon oxide films is greater than those found in polyethylene terephthalate.

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Interface Parameters of Si-SiO_2 Surface States Determined by the MOS Conductance Method

by

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Murray Hill, New Jersey

ABSTRACT

This is a progress report on a current study of interface state parameters in the Si-SiO_2 system using the MOS conductance method.[1] A brief review of this technique and the results of recent measurements will be given.

Prior to measurement, the only processing received by the samples was oxidation in steam or dry oxygen and the evaporation of gate electrodes. An attempt has been made to minimize the quantity of ionized impurities such as alkali metals which might be present in the samples by growing the oxide under bias.[2]

Electron capturing processes are measured on n-type and hole capturing processes on p-type silicon. The results for wet oxides are as follows. In the lower half of the band gap, there is a continuum of electron capturing states having a capture cross-section of 1.5×10^{-12} cm^2 and a continuum of hole capturing states having a capture cross-section of 5.4×10^{-16} cm^2. It is inferred from the magnitude of these capture cross-sections that the electron capturing states are positive before capture and neutral after, while the hole capturing states are neutral before capture and positive after.

In the upper half of the band gap there is a [illegible] of electron capturing states having a capture cross section of 1.5×10^{-15} cm^2. Because of the small capture cross section, it is likely that these states are neutral before capture and negative after.

The hole capturing states in the lower half of the gap and the electron capturing states in the upper half have densities which vary slowly with energy, the average density being 10^{11} $cm^{-2}-ev^{-1}$. These states have a distribution of time constants about a common one at each value of applied bias. By contrast, the electron capturing donor states in the lower half of the gap have a density which increases sharply from 6×10^{10} $cm^{-2}-ev^{-1}$ at mid-gap to 5×10^{11} $cm^{-2}-ev^{-1}$ 0.3 volts from mid-gap. Also, these donor states have a single time constant at each value of applied bias. The distribution of time constants for the neutral capturing centers is found to be log normal. Such a log normal distribution could arise from a normal distribution in surface potential. It could also arise if the states were normally distributed into the oxide so that majority carriers would have to tunnel to them.

For a dry oxide, the density of donors as well as the density of the neutral centers, are greater by an additional 10^{12} $cm^{-2}-ev^{-1}$ than a wet oxide.

REFERENCES

1. E. H. Nicollian and A. Goetzberger, "Measurement of Fast Surface State Parameters by the MOS Conductance Method", presented at the 1965 Solid State Device Research Conference.
2. A. Goetzberger, Jour. Electrochem. Soc., Vol. 112, July 1965, p. 1500.

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[illegible] IN THE [illegible] FIELD OF MOS CAPACITORS

by

A. Goetzberger
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Murray Hill, New Jersey

ABSTRACT

The MOS capacitance of p-type silicon in the inversion range is governed by lateral current flow in the channel. Bias aging of devices contaminated with alkali ions enhances the degree of inversion under the field plate due to ion migration. The MOS curve after aging can take on different shapes dependent on whether pinch-off occurs uniformly under the field plate (case 1) or in the fringing region at the edges of the field plate (case 2).

In the first case the MOS curve is shifted to more negative voltage without change of shape. In the second case, the pinch-off voltage remains low which leads to a broad valley of the MOS curve. Both curve shapes and transitions between them have been observed experimentally. For case 2 the peak of the equivalent parallel conductance is higher than before drift as is expected when pinch-off occurs in a ring shaped region at the periphery rather than under the entire field plate.

The field at the Si-SiO_2 interface as a function of distance from the edge of the field plate can be calculated as

a typical case of the following field of a plate condenser. For devices with valley broadening the exact location of the pinch-off point can thus be obtained. Its distance from the field plate is usually less than the oxide thickness. The surface charge concentration profile is therefore very steep.

Devices exhibiting curves without valley broadening (case 1) must have a wider spreading of impurities. This type of curve which is an exception rather than the rule is frequently obtained after certain chemical surface treatments of the oxide such as etching before evaporation of the contacts. Incorporation of aluminum into the oxide also leads to type 1 curves.

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SURFACE STATES AT STEAM-GROWN SILICON-SILICON DIOXIDE INTERFACES

by

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Murray Hill, New Jersey

ABSTRACT

A method of determining the energy distribution of surface states at silicon-silicon dioxide interfaces by using low-frequency differential capacitance measurements of MOS structures is described. Low-frequency measurements make it possible to determine the silicon surface potential as a function of MOS voltage directly from the experimental data without requiring knowledge of the Si doping profile. No graphical differentiations are required to determine the surface state density from the experimental curves, and errors introduced by uncertainties in the silicon doping density are reduced. In addition, it is shown that the measurements can be used to determine the relative lateral uniformity in the characteristics of the oxide and interface under the MOS field plate. Nonuniformities result in large errors in the surface-state density derived from MOS capacitance measurements. Measurements are presented and interpreted for both n- and p-type silicon samples prepared by bias-growing silicon dioxide on the silicon in steam.

STUDIES OF SODIUM IN SiO_2 FILMS BY NEUTRON ACTIVATION AND RADIOTRACER TECHNIQUES

by

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Murray Hill, New Jersey

ABSTRACT

Neutron activation analysis was used to detect sodium contamination on and in SiO_2 films and silicon substrates. Tracer sodium was diffused or drifted into SiO_2 films.

In the activation experiments oxidized silicon slices were irradiated with thermal neutrons at a flux of $10^{13}/cm^2$ sec. for 2-3 days in a water-cooled hole. The samples were then analyzed by progressive washing and etching and counting on the 1.37 or 2.76 Mev gamma peaks of Na^{24} (15 hr. half-life). A weighed sample of Na_2CO_3 was included for calibration.

The results of four of the activation runs may be summarized as follows:

Total Initial Na: $3 \times 10^{12} - 4 \times 10^{14}/cm^2$

Na inside films (6000A° thick): $\leq 3 \times 10^{12}/cm^2$

$\leq 5 \times 10^{16}/cm^3$

Na in silicon substrates: $1 \times 10^{14} - 1.5 \times 10^{15}/cm^3$

Most of the initial sodium activity was removed by washing or light etching (~ 200A°). The amount remaining inside the films was at or below the limit of detection in experiments to date. Experiments in progress may improve the accuracy of this determination. There was evidence that the total sodium concentration was sensitive to pre-oxidation cleaning, furnace cleanliness and subsequent handling of the slices. However, the silicon used in these experiments did not seem to be a significant source since sodium concentrations were usually lower in unoxidized silicon slices than in oxidized substrates.

Neutron activation evidence relating to phosphate glass is inconclusive as yet. In one experiment sodium diffused through a phosphate glass layer during activation at elevated temperature, but this may have been due to bombardment damage effects on the glass. Tracer experiments (below) have shown definite segregation of Na in phosphate glass layers.

Tracer experiments were carried out with Na^{22} (2.58 year half-life). Uniform layers of NaCl were deposited by evaporation. Thermal diffusion into 6000A° SiO_2 films at 600°C for 22 hours produced distributions which were high near the outer surface (~ $10^{19}/cm^3$), low in the middle region ($4 \times 10^{17} \rightarrow 1 \times 10^{17}/cm^3$) and had a slight upturn at the silicon interface.

Under the same diffusion conditions but with a phosphate glass layer on the SiO_2, penetration of sodium into the SiO_2 layer was drastically reduced, about 95% being held in the glass layer, as defined by etching rate, and little if any detectable beyond 1500A° from this point. None of the initial sodium activity could be washed off the outer surface of the phosphate glass whereas about two-thirds of it could be removed from the untreated SiO_2 surface by washing. The deposited sodium had been absorbed and largely stopped in the phosphate glass during the 600°C heat treatment.

A few attempts at 400°C for 1 hour have not shown any detectable thermal diffusion of sodium into SiO_2.

Drifting under gold dots, however, (1 min, 4V, 400°C) produced a sodium distribution tilted high at the silicon interface ($\sim 10^{20}/cm^3$). In this experiment, M. Yamin charged 31 out of 40 square dots in an irregular pattern. After washing and removal of gold, a radioautograph showed sharp images of the dots which had been charged, and no other activity. Ten percent of the activity was found within 2500A° of the outer surface and 90% within 800A° of the silicon interface. Total sodium corresponded to about 25% of the total charge introduced.

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Sodium Distribution in Oxide by Radiochemical Analysis and Its Effect on Silicon Surface Potential

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Radioactive Na^{24} distribution has been measured and correlated with MOS electrical data in over 40 samples of 6000 Å of SiO_2 grown by conventional wet and dry oxidation of 10 ohm-cm phosphorus doped silicon. Neutron activation by a high flux of thermal neutrons at 50°C maximum showed that Na was present in "clean" oxide in concentration 10^{16}—10^{17} cm^{-3}. Other impurities detected were Au and Phosphorus.

Sectioning was done by etching. Planarity of sectioning was verified by uniformity of interference colors. Gamma-ray spectrometry and both radiotracer Na^{24} and neutron activation were used. Sections as thin as 250 Å could be counted.

Neutron activation after drift showed residual Na piled up within a few 100 Å of the Si/SiO_2 interface. This interface concentration correlated with MOS flat band voltage shift, ΔV. High surface Na concentration resulted in a roughly U-shaped concentration profile.

Deliberate contamination with Na^{24} chloride, hydroxide, and bromide was used to obtain greater sensitivity. The U-shaped profile was seen after drift at 140 and 200°C and diffusion at 300 to 1000°C. Again ΔV correlated with Na piled up within a few 100 Å of Si/SiO_2. Kinetic studies showed that the profile was established within one minute, with concentration subsequently building up more slowly, giving rise to the observed ΔV (t). Time dependence was observed in diffusion at 500 and 800°C, which is not expected from the reported fast diffusion of Na. The anion was seen to have a significant effect in determining concentration profile and kinetics.

Surface $P_2O_5 \cdot SiO_2$ formed at 950°C was shown to accumulate Na from the SiO_2 and suppress the pile-up at the Si/SiO_2 interface.

The results suggest that Na is present in oxide grown with clean techniques and can account for observed instability. There appears to be a rate limitation at the air/SiO_2 interface, "pipes" through the oxide, appreciable neutralized Na in the oxide, Na^+ at the Si/SiO_2 interface, and enhanced solubility for Na at this interface.

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MAJORITY CARRIER SURFACE MOBILITIES IN THERMALLY OXIDIZED SILICON

V.G.K. Reddi

ABSTRACT

Majority carrier effective and field-effect mobilities in both n and p type silicon have been investigated using a novel technique. It was found that mobility is a continuously decreasing function of surface potential in contrast to the constant mobility observed by Leistiko et. al.* for carriers in the inversion regions over a considerable range of surface potentials.

Effects due to chargeable surface states have been considered and it was found that they do not contribute significantly to the changes in charge at the interface.

*Electron and Hole Mobilities in Inversion Layers on Thermally Oxidized Silicon Surfaces - O. Leistiko, Jr., A. S. Grove and C. T. Sah; IEEE Trans on Elec. Dev. P 248 Vol. ED-12, No. 5. 1965

A MODEL FOR RADIATION DAMAGE IN MOS STRUCTURES

A. S. Grove, E. H. Snow, A. Ballionoff

Experiments dealing with the effect of ionizing radiation in MOS capacitors and transistors are described. It is shown that if positive bias is applied to the gate during irradiation, very large shifts in the characteristics are observed, corresponding to up to $+10^{13}$ electronic charges built up in the oxide/cm^2.

A model is developed to account for these observations, and is compared with the experimental results. It is shown that the model predicts the time and voltage dependence of the damage in excellent agreement with the experiments. In addition, it yields a structual parameter which is expected to facilitate comparison of experimental observations made with different MOS structures.

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On The Nature of Oxide Charge Produced by Low Energy Electron Bombardment of Al-SiO_2-Si Capacitors

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It has been reported that low energy electron irradiation of MOS structures introduces positive charge in the oxide which can be detected by high frequency capacitance measurements. Continuation of that work reveals that a phosphorus glass (PG) interlayer between the aluminum and the oxide enhances the quantity of induced charge produced by a given primary electron flux in comparison with the analogous case of no phosphorus glass (NPG). Temperature-bias tests show that the bombardment produced charge is not mobile and undergoes no detectable interaction with mobile ionic species in the SiO_2 or with the dipolar species of the phosphorus glass. After heating at moderate temperatures with the structure shorted, the amount of positive charge detected by the C-V method can be decreased to nearly zero. After large negative metal-silicon bias at high temperature, the positive charge is then detectable. The effect suggests tunneling between deep oxide sites and the silicon surface. The behavior of insulators prepared by various oxidation techniques (plasma, anodic and wet or dry thermal oxidation and pyrolytic decomposition of silane) have been examined. Measurements have also been made on commercially available stable MOS structures to determine the role of irradiation in that case.

[illegible] VOLTAGE CHANGES IN MOS TRANSISTORS

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When p-MOST's are subjected to stress at elevated temperatures and positive gate bias one expects that the threshold voltage will increase if there are mobile positive charges in the oxide and remain constant if there are no such mobile charges. We have observed the reverse effect, i.e. a steady decrease in threshold voltage with stress time, in a number of p-MOST's.

Gate voltage to obtain a specified drain current at V_{DS} = 10V was measured at intervals during the test, cooling the unit to room temperature with bias applied after each stress interval. After stress the transfer characteristics were normal except for the decrease in threshold voltage. The leakage resistance was found to be lower by several orders of magnitude with the gate positive than with the gate negative.

These results are consistent with a hypothesis which postulates the existence of weak points in the oxide which are easily penetrated by the aluminum under the stress conditions. Penetration of the aluminum through the weak points reduces the effective oxide thickness, accounting for the gradual reduction in threshold voltage. The aluminum can form small local rectifying metal-semiconductor contacts with the n-Si, accounting for the non-symmetrical leakage.

These observations show that it is not sufficient merely to measure transfer characteristics in order to determine the degree of stability of MOS devices under stress. The transfer characteristic can change in either direction, so that the net result may be the difference of the effects of two competing mechanisms. Other measurements, such as leakage and capacitance, are needed to separate out the possible change mechanisms. One also needs to be careful in interpreting results of transfer characteristics measurements in terms of oxide-silicon interface state parameters.

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ABSTRACT

RADIATION DAMAGE IN MOS TRANSISTORS

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[illegible] changes in MOS device characteristics produced by neutron irradiation from the Northrop TRIGA reactor have been observed. [illegible] damage mechanisms have been identified: an increase in net [illegible] state density, a decrease in substrate resistivity, and a [illegible] in carrier mobility in the channel. The surface effect is [illegible]ally dominant, although the bulk resistivity effect becomes increasingly important as the resistivity of the substrate is increased. An exact closed form expression for the turn-on voltage has been derived by obtaining a solution to Poisson's equation in the gate region. The open circuit gate to substrate capacitance as a function of gate to substrate voltage has been obtained by numerical integration techniques in terms of the charge density and dielectric constants present in the Si[illegible] layer and Si substrate. For both enhancement and depletion devices, an increase in positive charge [illegible] is due to creation of mobile positive ions, and that the [illegible]ing net accumulation rate with increasing flux is due to a [illegible]ation or recombination process competing with the creation [illegible]. On this basis, a rate effect is expected.

[illegible] degree by which the experimental results are affected by [illegible] radiation coincident with the neutrons is difficult to [illegible]mine. This uncertainty will be resolved by running control [illegible]s in a pure γ radiation environment and by changing the reactor [illegible]eration to γ ratio in the next test series.

Exposure of an MOS transistor to a pulsed ionizing radiation environment results in a significant transient drain current. The transient drain current is the result of the radiation-induced carrier generation in the bulk semiconductor material and charge scattering in or out of the metalic gate contact. In the common-source configuration, the transient drain current will include the

photocurrent of the reverse-biased drain-substrate junction and the secondary drain photocurrent resulting from the change in charge on the gate-source capacitance. A fraction of the carriers generated in the channel region will be swept to the substrate junction resulting in a gate displacement photocurrent. The quiescent gate voltage will be decreased by the ohmic drop of the photocurrent through the source resistance. As the gate voltage is decreased, the depletion layer width changes causing a secondary drain photocurrent. In the enhancement-type device, the secondary drain photocurrent will be in the direction to decrease the quiescent drain current. The second source of secondary drain photocurrent results from the net charge scattering from the metallic gate. Electrons ejected from the case of the transistor will be scattered into the base region and photons reaching the base contact will scatter electrons out of the metalic gate. The net change in charge will also change the quiescent gate voltage inducing a secondary drain photocurrent.

Pulsed-radiation transient responses of MOS transistors have been studied experimentally in a high intensity 600 kv flash x-ray machine. Common-source transient drain currents of both enhancement and depletion type devices have been measured as a function of the external gate resistance and the quiescent drain current. Experimental results can be favorable compared to the analytical results obtained from a first-order modification of the small-signal transistor model.