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ORIGIN OF INTERFACE STATES IN SILICON/ SILICON-DIOXIDE SYSTEM - A PIEZOELECTRIC MODEL

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ABSTRACT

The need for higher manufacturing yields and improved operational reliability of Semiconductor Devices and circuits has led to a continuing scrutiny of all processing steps of these Devices. Just like in the bulk of semiconductor, allowed states also occur at the surface of a semiconductor within the energy gap, which are called surface states. A third type of states, similar to surface states, occur at the interface of Si/SiO_2 system. These states are called interface states. Very often they are simply called surface states. The origin of these states is much less understood than that of bulk states.

There is as yet no satisfactory theoretical model for explaining the existence of interface states at Si/SiO_2 interface of MOS Devices. These interface charges have been found to vary, among other things, with the oxide thickness, oxidation temperature and substrate thickness. Since the greatest body of scientific and technological work has been carried out on silicon, Si/SiO_2 interface will be treated predominantly in this present investigation.

A model, based on the piezoelectric response of SiO_2 to thermally-induced external stress assumed to be present during fabrication, has been developed to investigate existence of interface states at Si/SiO_2 interface. To confirm this idea the interface charge density has been computed. The model predicts variations of interface charge density with oxide and substrate thickness which fairly explains the experimental results.

INTRODUCTION

Studies on the surface properties of Metal - Oxide Semiconductor (MOS) structure have been reported by several workers (1-5). As a result of extensive studies using mainly MOS capacitors, MOS transistors and gate controlled diodes, the Si/SiO_2 interface is probably the most well characterized solid - solid interface (6). It is well known that the thermally grown oxide layer on silicon surface is characterized by positive charge in the oxide layer. Deal et. al (7) have indicated that the charge centres are located near Si/SiO_2 interface and the surface states density is not a function of the resistivity of the material. However, the surface charge is found to depend upon the oxide thickness, the oxidation temperature and the annealing treatments. Brotherton et. al. (8) have given experimental results of surface charge and stress in the Si/SiO_2 system. However, in spite of the large volume of work, no satisfactory model has emerged which fully explains the variation of interface charge with oxidation temperature. To reach a better understanding of the basic mechanism involved in the theoretical study of the surface states density, a phenomenological idea is used in which the silicon dioxide has been treated as a piezoelectric material. In the present communication, surface state density has been computed using beam theory and bimetallic strip theory considering SiO_2 a piezoelectric material.

The previous authors (9-11) were of the opinion that piezoelectricity is an inherent property of the crystalline structure, but the work of Murayama (12) indicates that charge injection from the electrodes and their subsequent trapping in the film might be responsible for this effect. Singh et. al(13) in their study on MGOS has shown that SiO_2 can get polarized under electric field at suitable temperature. It has also been shown by Sussner and Drausfeld (14) that PVF_2 film, though glassy in structure, does show piezoelectric character.

TYPES OF INTERFACES

Defects present in the oxide which appear to have a net positive charge is generally named fixed oxide charge. Although at room temperature these centres do not interact with mobile carriers at the silicon surface, they still induce undesirable conducting n-type channels on the surface of the p-type silicon. It has been suggested by Grove et.al. (3) that these centres can increase the radiation sensitivity of the oxide.

The achievable interface-state density has continuously dropped (15) which has been shown in Fig.1.

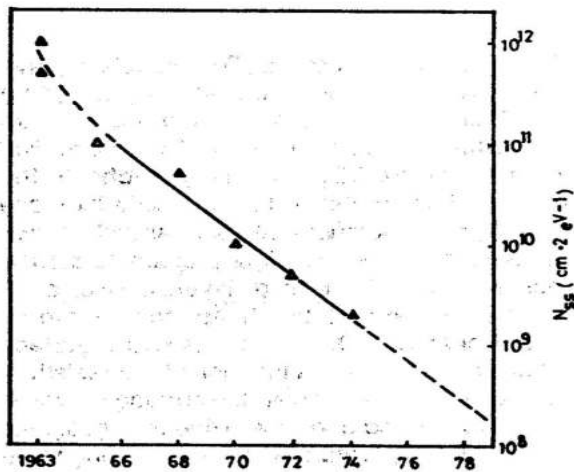


Fig.1: Variation of interface state density with time

The observed improvement in the density has been achieved entirely by empirical methods, without recourse to scientific models of interface states. The improvement is necessary because a low interface-state density is of crucial importance for semiconductor devices. The major spur towards improvement of interface quality has been the MOS technology, which is now in a very advanced state. For most of the MOS devices the present achievable level of interface-state density is more than adequate. However, further improvement is necessary for advanced types of devices, such as charge coupled devices (CCD). There are two different types of interfaces.

1. Interface without states - Intrinsic interface
2. Interface with states - Extrinsic interface

INTRINSIC INTERFACE

For the ideally oxidized SiO_2 - Si interface, it can be imagined that all dangling bonds which cause a high interface state density in the case of a free silicon surface are saturated by bonds with oxygen (16, 17). The strong binding energy of oxygen to silicon shifts the energy of the bonds to lower energies away from the window of the silicon band gap where they are measured electrically (18). It is therefore plausible that the electrically measured SiO_2 - Si interface density is very low, far less than the number of atoms or bonds in the interface. However, it can be easily shown in the schematic arrangement of the bonds in the two dimensional drawing. Fig.2,

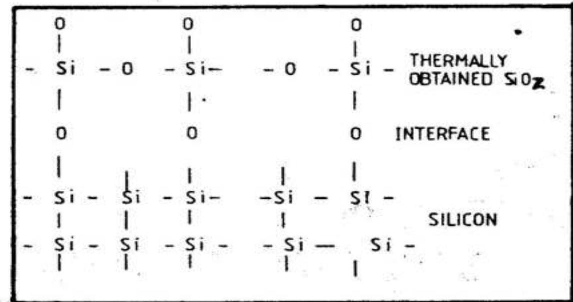


Fig.2: Systematic arrangement of bonds in Si/SiO_2 system

which can be used to represent the 3-dimensional tetrahedral configuration, that the wide lattice of the SiO_2 does not match the lattice of Si. The intrinsic interface states depend mainly on oxidation conditions for thermally oxidized silicon. Dominant parameters which control the interface properties are the technological parameters for the oxide growth. The oxide growth, in the oxidation process of Si, proceeds in three steps (19):

(i) Oxygen transfer into the oxide already formed
(ii) Diffusion of oxygen through the oxide
(iii) Formation of SiO_2 due to reaction of oxygen with silicon at the interface.

Oxidation of Si at higher temperatures (> 1000°C) is diffusion controlled which leads to a square root law for oxide growth. At lower temperature (< 1000°C) the growth is controlled by surface reaction which leads to a linear growth rate. Both types of reactions lead to a thin region of SiO_2 containing partially ionized silicon near the Si/SiO_2 interface where diffusing oxygen reacts to form new SiO_2. There is a thin region with a reduced oxygen concentration(20). The relation of interface states with the oxidation temperature has been explained by Deal (19) and is shown in Fig.3.

A high interface state density is obtained by low-temperature oxidation because there are many unsaturated silicon bonds produced by the slow reaction rate (Fig.3a). A low interface state density is obtained at high temperature because the reaction there is high enough to dominantly produce SiO_2 (Fig.3b). The same low interface state density can be obtained by annealing a low-temperature oxide having excess oxygen (Fig.3c). The annealing, however, must not be too long to avoid depletion of oxygen. Goetzberger et. al. (21) have suggested a 'Charge Model' to interpret interface states. This model explains fast interface states by the binding of mobile charge carriers in the semi-

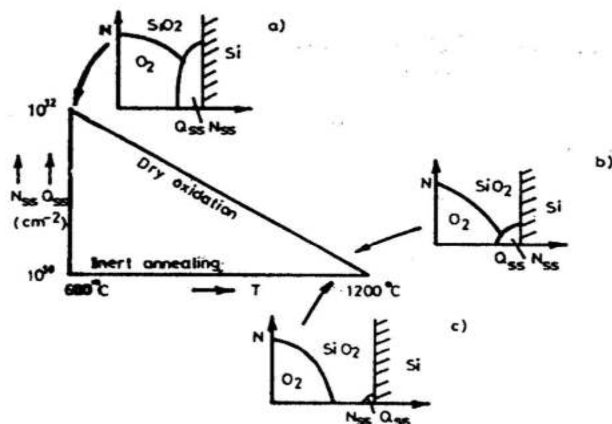


Fig. 3: Relation of interface states with oxidation temperature

conductor to charge centres in the oxide in the immediate vicinity of the interface by Coulomb attraction. A positive charge centre in the oxide will give to a bound donor state analogous to that found in bulk silicon. A negative charge centre will cause an acceptor state.

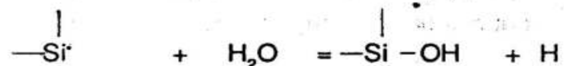
The random distribution of the depth of the charge centres in the oxide and the partial overlap of their potential will smear out the distribution of the bound states. Centres located deep in the oxide from the state closer to the band edges. Overlapping charges produce deep states. When the energy position is deeper than O.1ev, a distribution of interface states with a high density near the band edges and a drop-off towards midgap is expected.

EXTRINSIC INTERFACE

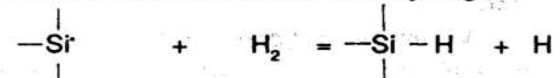
Impurities may enhance or compensate the oxide charge as well as the number of fast interface states. The property of the impurity depends on its electrical and chemical nature and also its mobility in the interface region. Many elements have a tendency to be gettered in the disturbed region near the interface so that they accumulate in this region even if they are only present in a small concentration.

All the alkali impurities cause a positive space charge in the oxide in the vicinity of the Si/ SiO_2 interface. Normally, not all of the impurity atoms are electrically active. An increase of the interface state density proportional to the fixed oxide charge has also been reported. This result supports the "Charge Model' discussed for intrinsic interfaces. However, the increased interface state density could also be caused by additional strain in the Si/SiO_2 interface.

A pronounced effect on interface states is observed for oxidation or annealing in presence of hydrogen (17, 22). These effects can be described by a chemical reaction of unsaturated silicon bonds with water at elevated temperatures under formation of silanol group (22).



A similar reaction is obtained for hydrogen



At temperatures below 500°C annealing in an ambient containing water or hydrogen leads to a reduction of the interface state density. At high temperatures, the reaction is reversed and the interface state density is increased again (22). By varying the partial water pressure, the reaction can be weighted to one side or the other. In presence of hydrogen or water, the annealing triangle is not valid any more because the reaction of hydrogen with oxide charge centres and interface states is different. The oxide charge decreases continuously during annealing even at high temperatures while the hydrogen bond of the above reaction splits again and causes an increase of the interface state density.

The behaviour of other elements is even less well understood. Chlorine itself has no effect on interface state density or oxide charge (23). However, it can be used to bind and neutralize sodium ions which cause an oxide charge (24, 25). Gold is a particularly significant impurity in silicon devices because of its pronounced effects on carrier life time. Gold is also gettered at the Si/SiO_2 interface region during oxide growth (26). It causes some positive space charge and a large interface state density, larger than the number of gold atoms at the interface (26). This behaviour has not been explained properly.

EFFECT OF VARIOUS STRESSES ON INTERFACE STATES

There are some interface states that occur through the preparation technology of the device, which are uncontrolled. Apart from interface states introduced during fabrication process reactive environment, irradiation with x-rays, exposure with light and ion-implantation also increase the distribution of the interface states density. Irradiation increases the thermal vibration of atoms that create electrons and holes in the interface region leading to a build-up of positive space charge in the oxide and increases the interface states density. The electrons drift out of the oxide layer but many holes become trapped. MOS devices with a thin oxide layer (100 A) show little charge trapping; that is,

the number of traps is reduced since holes mays be able to leave the thin-oxide-layer before they are trapped. Ionic implantation of impurities causes great changes at Si/SiO2 interface.

THEORETICAL CONSIDERATION

A linear elastic beam theory for an isotropic material (27) has been used to study Si/SiO2 system. In applying the linear elastic beam theory to Si/SiO_2 system, one can assume the origin of coordination at the Si/SiO_2 interface and adopt the convention that positive and negative stresses represent tension and compression respectively.

Stress on Si:

$$\sigma_{Si} = \frac{P(J)}{D1} + \frac{E1\,D1R(J)}{2}$$

Stress on SiO_2:

$$\sigma_{ox} = \frac{P(J)}{D2} + \frac{E2\,D2R(J)}{2}$$

where E1 - Young's Modulus of Si
E2 - Young's Modulus of SiO_2
D1 - Thickness of Si chip
D2 - Thickness of SiO_2 film

$$P(j) = 2[E1\ I1 + E2\ I2]\ R(j)/H$$

$$H = D1 + D2$$

$$R(j) = \frac{6(\alpha_1 - \alpha_2)(T - T_o)(1 - m)_2}{H[3(1 + m)^2 + (1 + mm)(m^2 + \frac{1}{mn})]}$$

α_1 - coefficient of thermal expansion for Si
α_2 - coefficient of thermal expansion for SiO_2

T - Oxidation temperature
T_o - Room temperature
m - D2/D1
n - E2/E1

I1 and I2 are moments of inertia of Si-chip and SiO_2 - film behaving as beams.

$$I1 = M1\ D1^3/12$$

$$I2 = M2\ D2^3/12$$

M1 and M2 are the masses of Si-chip and SiO_2-film respectively.

COMPUTATION OF INTERFACE CHARGE

From piezoelectronic consideration the charge on Si surface is expressed as (28)

$$Q_{ss} = P_Z\ \sigma_{Si}$$

where P_Z is the plezoelectric stress constant. The charge state density can be given by

$$Q_{ss} = Q_{ss}/q = P_Z\,\sigma_{Si}/q$$

q - electronic charge

The above discussed method has been used to compute the interface state density for Si/SiO_2 interface. The detailed computer program is given in Appendix 'A'.

RESULTS AND DISCUSSION

The stresses at the interface have been computed as a function of oxide and substrate thickness at 1200°C oxidation temperature. The results of these calculations have been plotted in Figs.4 and 5. For performing the calculations, the necessary physical parameters are given in Table 1 and the computed Q_{ss} in different conditions are given in Tables 2 and 3.

The model has been checked by calculating the variation of charge state density at the interface with oxide film thickness. Surface charge has been calculated for different oxide thickness at T = 1200°C and Si-chip thickness of 0.2×10^{-1}cm. Theoretically charge density is found to decrease with oxide thickness which agrees quite well with the experimental results (29). Experimentally the charge decreases with thickness up to 0.4×10^{-4}cm and afterwards it becomes approximately constant. The variation of surface state density with oxide thickness has been plotted in Fig.4.

The model was further checked by calculating the charge state density by changing the thickness of Si-chip. Fig. 5 shows that the charge state density is practically independent of the Si thickness which fairly explains the nature of experimental results (29).

The question of any inconsistency posed by the results can be eradicated by taking into account the dependence of piezoelectric constant P_z with temperature. P_z decreases by 17% as the temperature rises from 15 to 500°C (30). Hence if P_z is taken as a temperature dependent $P_z = P_z(T)$, the model would certainly explain the experimental results (22) with great accuracy.