

MOS Structure Undergoing F.N. Tunnel Injection Aging

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The behaviour of thin MOS structures under high electric field (= 10 MV/cm) and Fowler-Nordheim tunnel injection has been studied in correlation with various elaboration technologies. Several degradation mechanisms taking place both in the bulk of the gate oxide layer and at the interfaces have been characterized. Such intensive stresses induce a gradual degradation of the MOS characteristics and lead finally to a complete destruction of the structures. This aging is thought to be essentially controlled by interfacial phenomena involving formation of intrinsic defects.

§1. Introduction

In order to meet VLSI density, thinner and thinner gate oxide as well as reduced components area are required. With the present technology, the reliability of such thin SiO₂ layers remains aleatory¹⁾. The quality of the Si-SiO₂ interface appears to be of great importance. It is very controlled by the silicon substrate state (surface quality, orientation and doping), SiO₂ growth processes (dry or wet ambient environments, with or without HCl), and gate material (Al or Poly-Si)²⁾. In order to optimize the MOS elaboration technology, it becomes very important to analyze and explain the influence of these various parameters on aging mechanisms under intensive stresses.

§2. Sample preparation and experimental techniques

The thin oxide MOS structures we have studied have been elaborated on Phosphorus or Boron doped silicon wafers in the range 10¹⁵-10¹⁷ cm⁻³. The silicon crystal orientation is <100>. The gate oxide layer is between 10 and 50 nm thick whereas the field oxide thickness is greater than 100 nm. Aluminium or degenerate polycrystalline silicon are used as gate material.

Samples are subjected to an usual electrical characterization (C-V_G, admittance dispersion curves, Y(V_G, ω)) after each injection step. In order to overcome early breakdowns due to dioxide inhomogeneities like pinholes, a small capacitor area (< 0.07 mm²) is chosen to be tested.

Fowler-Nordheim injection can be performed either from the silicon substrate or from the gate depending on the gate voltage V_G. V_G is automatically reajusted in order to maintain a constant injection current density.

The regulated voltage (V_R=V_G) is continuously recorded during aging steps.

Typical V_R(t_{inj}) plots are shown on Fig.1 for Si→Poly-Si injection. There is coexistence of two traps filling mechanisms. One of them has an exponential evolution due to the filling of native traps i.e. defects existing prior to injection. This first mechanism is usually described by the following first order kinetic model :

$$\Delta V_{ex}(Q_{inj}) = \frac{q}{\epsilon_{ox}} \bar{x}_{ex} N_{ex} \{1 - \exp(-\frac{\sigma_{ex} Q_{inj}}{q})\}$$

where ΔV_{ex} is the regulated voltage increase in the case of an injection from the substrate, Q_{inj} the injected charge density, ε_{ox} the absolute dielectric permittivity of SiO₂, \bar{x}_{ex} the native centers centroid measured from the gate-SiO₂ interface, N_{ex} their density and σ_{ex} their capture cross section.

The second mechanism produces a linear increase of V_R owing to the filling of new defects induced by the injection stresses. These traps are filled as soon as they are created so only the voltage shift to saturation ΔV_{ind} during the injection can be detected. ΔV_{ind} can be described by the following equations :

$$\Delta V_{ind}^+ = r^+ \frac{x_{ind}^+}{\epsilon_{ox}} \cdot Q_{inj} \text{ for Si} \rightarrow \text{Gate injection}$$

$$\Delta V_{ind}^- = r^- \left(\frac{t_{ox} - x_{ind}^-}{\epsilon_{ox}} \right) \cdot Q_{inj} \text{ for gate} \rightarrow \text{Si injection}$$

where t_{ox} is the SiO₂ layer thickness. The proportional

factor r^+ or r^- represents the induced traps filling rate when injection is performed from the substrate or from the gate respectively, \bar{x}_{ind}^+ and \bar{x}_{ind}^- being the centroid of the distribution measured from the Gate-SiO₂ interface.

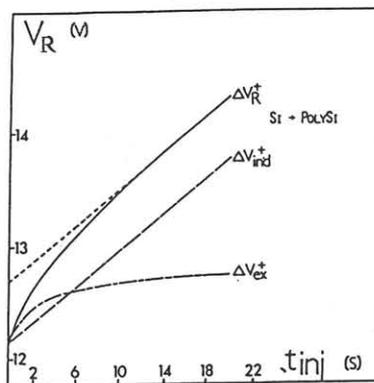


Fig. 1 - Typical $V_R(t_{inj})$ plots obtained for Poly-Si gate MOS structures with a 10 nm thick SiO₂ layer. The Si → Poly-Si injected current density is 0.64 A/cm².

We have developed an experimental procedure based on the exploitation of the regulated voltage evolution for both injection modes (case of a N type substrate). It leads to the determination of the traps parameters \bar{x}_{ind}^+ , r^+ , N_{ex} , \bar{x}_{ex} , σ_{ex} . The results obtained for a Poly-Si gate structure with a 10 nm thick SiO₂ layer are given on Table 1.

	NATIVE TRAPS			INDUCED TRAPS			
	Γ_{ex} cm ²	N_{ex} cm ⁻²	\bar{x}_{ex} t _{ox}	r^+	\bar{x}_{ind}^+ nm	r^-	\bar{x}_{ind}^- nm
P DOPED POLY-SI GATE	$4.7 \cdot 10^{-20}$	$1.7 \cdot 10^{12}$	0.4	$5 \cdot 10^{-8}$	1.5	$4.3 \cdot 10^{-8}$	2.3
AS DOPED POLY-SI GATE	$5.7 \cdot 10^{-20}$	$1.7 \cdot 10^{12}$	0.4	$3.2 \cdot 10^{-8}$	1.5	$4 \cdot 10^{-8}$	2.3

Table 1 - Native and induced traps parameters obtained for Poly-Si gate MOS structures ($t_{ox} = 10$ nm)

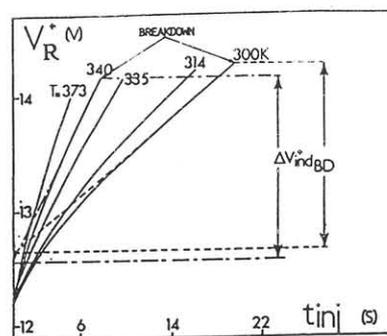
§3. Degradation phenomena

Regulated voltage and flat band voltage variations measurements as well as conductance and quasistatic curves have revealed various aging mechanisms.

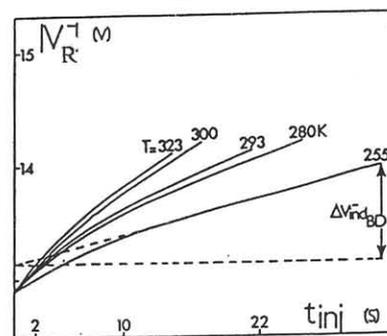
1. The filling of native capture centers in the bulk of SiO₂ induces an exponential variation of the regulated voltage. Very low capture cross-section between 10^{-18} and 10^{-20} cm² have been detected. Because of their low capture efficiency, these native traps have not a determinative influence on the MOS characteristics.

2. Creation and fast filling of new centers induced by

the injection stresses have been observed. They are formed near the cathode interface at less than 3 nm according to a thermally activated process as shown on Fig.2. Their density increases linearly as a function of injected charge up to destructive breakdown. Their concentration at breakdown time is temperature independent. The formation of these charged centers seems to be greatly involved in the breakdown process³⁾.



a)



b)

Fig. 2 - Curves showing the evolution of the regulated voltage V_R^+ during a constant injection current density ($J_{inj} = 0.64$ A/cm²) with the temperature T as a parameter. a. Case of the Si → Poly-Si injection. b: Case of the Poly-Si → Si injection

3. Injection stresses induce a gradual degradation of the Si-SiO₂ interface where slow and fast interface states are generated. The fast surface states capture cross section is about 10^{-15} cm². Their density N_{SS} increases as a function of injected charge N_{inj} according to the following law :

$$N_{SS} = R(N_{inj})^\alpha$$

The α exponent depends on the MOS elaboration process. For Poly-Si gate structures, it is approximately equal to 0.25. It reaches 0.75 for Al gates. The prefactor R is temperature and electric field independent. Slow states are induced at the Si-SiO₂ interface. They are thought to be of donor type and responsible of the observed C-V_G curves instabilities.

§4. Influence of elaboration parameters

Both the formations of fast and slow interface states are greatly influenced by the MOS elaboration parameters: SiO₂ growth environments and gate nature. Fig.3 compares the V_{FB} variation due to the generation of slow states and the evolution of N_{SS} for different samples⁴⁾. It appears that presence of Al has disastrous effects on the degradation rate. It could be due to migration of metallic ions through SiO₂ towards the Si-SiO₂ interface inducing the formation of new electrically active defects. V_{FB} negative shifts are minimum for Poly-Si gates and maximum for Al gates and wet oxides. It appears that the magnitude of interfacial charge is greatly enhanced by the presence of water in the oxidation ambient environment. Fig.3 also shows that the V_{FB} variations at breakdown time are approximately constant for all the samples. It could indicate a correlation between the breakdown process and the formation of the positive interfacial charge.

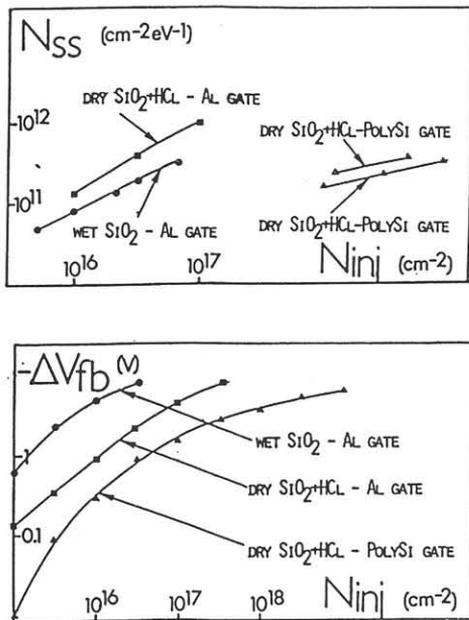
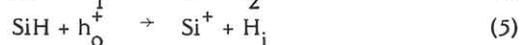
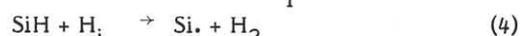
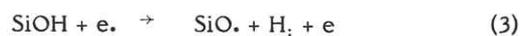
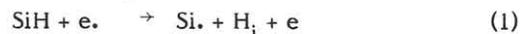


Fig. 3 - Fast interface states density N_{SS} and V_{FB} variations due to the formation of a positive interfacial charge as a function of injected electrons density N_{inj} . Comparison for different technologies which have been elaborated with various technologies.

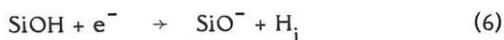
§5. Physicochemical mechanisms

Some experiments have shown that the V_{FB} variation due the positive interfacial charge depends on the SiO₂ layer thickness t_{ox} . A dependence of ΔV_{FB} on $(t_{ox})^2$ has been observed. Such a dependence is not necessarily a consequence of a uniformly distributed positive charge in SiO₂; furthermore, photocurrent

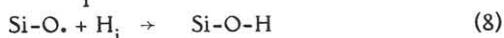
measurements have proved that this positive charge is located near the Si-SiO₂ interface⁽⁵⁾. It rather indicates a generation process which is initiated in the bulk of SiO₂. For example, a chemical species could be created, then diffuses to the interfaces and generates interface states by an unknown mechanism. The density of the generated interface states is then related to the number of released chemical species in the bulk of SiO₂. The influence of water on interface state generation suggests that the physicochemical processes are essentially controlled by hydrogen related species⁽⁶⁾. Evidence of hydrogen in SiO₂ films has been proved by several direct and indirect methods. Direct analysis techniques such as radiative analysis, infrared spectroscopy, nuclear reaction⁽⁷⁾ have shown that high concentrations of hydrogen related compounds exist in the bulk of SiO₂ and at the Si-SiO₂ interface⁽⁸⁾. Infrared absorption spectroscopy analysis has revealed high densities of SiH groups piled up near the silicon surface. The presence of OH groups bonded to a silicon atom (SiOH) or to an hydrogen atom (H₂O) has also been brought to light. SiOH behaves as an electron acceptor whereas SiH acts as an electron donor (hole trap)⁽⁷⁾. Another important difference between SiOH and SiH is that the SiH bond is weaker than either the Si-O or O-H bond and therefore, is the more easily broken by several stresses (irradiation, heat treatment, electric field, injection). SiH and SiOH dissociation reactions at the Si-SiO₂ interface result in the generation of trivalent silicon atoms Si[•] or oxygen dangling bonds SiO[•], which are electrically active defects. These reactions could be the following ones⁽⁹⁾.



$e.$ is an energetical injected electron which is able to break the Si-H or Si-O-H bonds. Si[•] and SiO[•] act as fast interface states. Si⁺ trivalent silicon atoms are assumed to form the observed positive interfacial charge generated during injection stresses. These defects are able to exchange electrons with the silicon substrate by tunneling transitions. They act as slow interface states and produce great instabilities of the MOS structures characteristics. H_i is an interstitial hydrogen which is released during reactions (1), (3) and (5). It can be also released in the bulk of SiO₂ subsequently to the trapping of injected electrons by hydroxyl groups:



H_1 can diffuse towards the Si-SiO₂ interface. The migration process of the atomic hydrogen during electron injection is more complicated than the normal diffusion or drift processes for the two following reasons. First, there are high densities of electrons in the oxide during injection. The presence of electrons may affect the transport mechanism of H_1 . Secondly, the atomic hydrogen may react with silicon dangling bonds or nonbridging oxygen in the oxide to form some intermediate states :



Subsequently, the energetic electrons will break the Si-H or Si-O-H bonds and release the atomic hydrogen. When H_1 reaches the Si-SiO₂ interface, it can have two antagonist effects. According to reaction (4), it can react with SiH bonds and form active trivalent silicon atoms. On the other hand, it can annihilate these same defects :



The formation of surface states appears to be greatly influenced by hydrogen related species. The rate of generation depends on many parameters : water related species concentrations, SiO₂ electric field i.e. hot electron energy, and injected current density. It is controlled by the slowest physicochemical processes, i.e. either by the chemical reactions occurring at the Si-SiO₂ interface or by the diffusion speed of H or OH atoms in SiO₂^{10,11}). Assuming that the rate of interface states formation is limited by the diffusion process of OH atoms from the interface towards the bulk of SiO₂, Jeppson et al.¹⁰ have shown that the N_{SS} variation is proportional to $(N_{inj})^{1/4}$. This result has been confirmed by our experiments for Poly Si-gate structures. The faster increase of N_{SS} for wet oxides must be due to a higher concentration of hydrogen related species in the bulk of SiO₂ and at the Si-SiO₂ interface.

Another point which has been revealed by our experiments is a possible correlation between the formation of the interfacial positive charge and the breakdown process. For the case of SiO₂ thin films ($t_{ox} < 20$ nm), a model for impact ionization and breakdown cannot be reasonably described as an avalanche theory. Production of electron-hole pairs by impact ionization is insufficient, as shown by Di Stefano et al.¹²). Generated holes during injection could be drained towards the cathode interface by the electric field and captured by hole traps resulting in the formation of a positive charge (reaction (5)). Maserjian et al.¹³ have suggested that the

generation of positively charged states near the Si-SiO₂ interface causes a distortion of the electric field in SiO₂, and a corresponding increase in the injected cathode current which leads to an increase in the rate of impact ionization. Then, great positive charge densities near the injecting interface could be sufficient to induce internal electric field high enough to break Si-O bonds and to initiate the breakdown process.

§6. Conclusion

Thin oxide MOS structures aging under high electric field is essentially controlled by interfacial phenomena involving formation of intrinsic defects. These defects act as donor like slow states when they are located near the Si-SiO₂ interface and can exchange charge carriers with the silicon substrate. They are responsible for the great instabilities of the MOS electrical characteristics. Water related species concentration in the bulk of SiO₂ and at the interfaces appear to be a very important parameter in the degradation processes. Breaking of Si-H or Si-OH groups results in the generation of positively charged defects and of fast interface states. The destructive breakdown process in thin SiO₂ films seems to be greatly correlated to the formation of this positive interfacial charge.

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