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An AES study of damage induced by inert gas ions at SiO₂ surfaces : influence of ion mass and energy

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Résumé. — L'endommagement de surfaces de SiO₂ bombardées avec des ions Ar⁺, Ne⁺ et He⁺ d'énergie 70-500 eV est étudié par spectroscopie Auger dans des conditions d'analyse non destructives. La couche perturbée est déficiente en oxygène et contient de nouveaux états de liaison du silicium, caractérisés par les pics SiO_x (82 eV) et Si (89 eV). Les modifications observées en fonction de la masse et de l'énergie des ions renseignent sur le mécanisme de l'interaction ion-surface. A énergie moyenne (500 eV), le changement de composition est compatible avec un modèle de pulvérisation par collisions élastiques. A basse énergie (80-250 eV), l'interaction de He⁺ est totalement différente de celle de Ar⁺ et Ne⁺, ce qui suggère l'entrée en jeu de processus inélastiques du type neutralisation Auger.

Abstract. — The altered layer produced by sputtering SiO₂ with Ar⁺, Ne⁺ and He⁺ ions of 70-500 eV energy is studied by AES in conditions avoiding electron beam damage. The understoichiometric layer is characterized by an attenuation of the O KVV Auger peak and by the appearance of additional SiO_x (82 eV) and Si (89 eV) peaks in the Si LVV spectrum. The dependence of this damage upon ion mass and ion energy gives information on the mechanism of ion-surface interaction. At medium energy (500 eV), the change in surface composition is compatible with a collisional sputtering model. At lower energies (80-250 eV), He⁺ interacts quite differently from Ar⁺ and Ne⁺, suggesting the onset of inelastic processes like Auger neutralization.

1. Introduction.

The present work is part of a systematic study of radiation damage at oxide surfaces, induced by inert gas ions with energies typical of sputter-cleaning and by electrons with energies typical of AES, i.e. energies which the particles may possess in a cold plasma environment. The Auger probe itself may have a damaging effect, so that one has to discriminate between true ion beam damage and additional damage due to the electrons.

Once the operating conditions for least-damaging analysis are determined (fluence : $< 10^{18}$ e/cm² [1], energy : 2 500 eV [2]), one may isolate the changes due to the sole ion bombardment and investigate their dependence upon ion mass and ion energy. This is what we attempt here.

2. Experimental.

The Auger analysis is performed with a single-pass CMA in an ultra-high vacuum chamber, which is separated from the ion pump by a gatevalve.

The ion gun is of the « ion gauge » type. It is operated in the static mode : 10^{-4} torr inert gas, ion pump isolated, Ti sublimation pump on to keep the residual pressure of active gas low. Typical working conditions are : 70-500 eV ion energy, normal incidence, $1-10$ μ A/cm² ion current density. The fluence used corresponds to damage saturation, respectively : 4×10^{15} (Ar⁺), 2×10^{16} (Ne⁺) and $1-2 \times 10^{17}$ (He⁺) ions/cm² [1]. After completion of the bombardment, the inert gas is pumped away *via* an auxiliary UHV diffusion pump before reopening the ion pump. In this way, the pressure is back in the low 10^{-9} torr range two minutes after the end of the bombardment. Rapid cycling between bombardment at 10^{-4} torr and analysis at 10^{-9} torr is thus allowed without overloading the ion pump with inert gas.

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Typical operating conditions for Auger work are : primary energy 2 500 eV, primary current 10^{-7} A, modulation $2 V_{p-p}$, scan speed 25 eV/min, time constant 0.3 s. The duration of a scan corresponds to a fluence of less than 10^{18} e/cm². The nominal beam diameter is 0.1 mm ; the current is measured with the sample holder biased + 90 V relative to ground.

The SiO₂ sample is a 3 500 Å thick dry oxide grown on Si (of the same type as used in Refs. [1, 2]). It is mounted on a Ta-covered NB block heated by a W resistor. The reference state (« undamaged » surface) is obtained after 5 min annealing at 700 °C in the UHV ambient [1]. Notice that the sample « history » (numerous sputtering + annealing cycles) is markedly different from that of a sample only sputtered and never heated. While this may affect macroscopic properties, we have no evidence that the surface composition would be different.

3. Results.

AES gives evidence for ion-induced damage at SiO₂ surfaces in the form of compositional changes (peak height, peak shape) and electrical changes (peak displacement due to charging) [1, 2]. Here, we restrict ourselves to the former type of changes. The modifications are evaluated with respect to the reference spectrum, which is regenerated by annealing before each new ion bombardment. All results given below relate to the freshly ion-bombarded surface with minimum electron beam exposure.

Changes typical of ion bombardment consist in a slight attenuation of the O KVV peak (502 eV) and large changes in the Si LVV spectrum (Fig. 1) whereby the SiO₂ peak (77 eV) loses intensity at the benefit of new features appearing on its high-energy wing near 82 and 89 eV. The 89 eV peak is called « free Si » or « elemental Si » peak ; the intermediate 82 eV peak is called « SiO_x peak ». Further exposure to the electron beam (Fig. 1c) would lead to the decay of the SiO_x peak and the growth of the Si peak.

3.1 IONS OF SEVERAL HUNDREDS OF eV. — The O KVV peak suffers an attenuation, which depends on the nature of the projectile. For 500 eV ions, we find mean attenuations rising with decreasing mass : 7 % (Ar), 11 % (Ne), 17 % (He).

Turning to the Si LVV spectrum, we investigate the behavior of the damage features (SiO_x and Si peaks) as a function of the main parameters of the ion bombardment (fluence, energy, mass). We note (Fig. 2) that the SiO_x peak appears for lower fluences than the Si peak. Taking the example of Ne⁺ ions where the saturation fluence is 2×10^{16} ions/cm² [1], the SiO_x peak is already detected (Fig. 2) for 5×10^{14} ions/cm², while the Si peak appears around 3×10^{15} ions/cm², i.e. respectively 2.5 % and 15 %

Fig. 1. — Si LVV Auger spectra of SiO₂ surfaces : (a) undamaged ; (b) freshly bombarded with 250 eV Ne⁺ ; (c) as (b), but with additional 15 min exposure to the electron beam. Mod. $2 V_{p-p}$, 2 500 eV electrons.

Fig. 2. — Modification of Si LVV Auger spectrum of SiO₂ as a function of ion fluence (Ne⁺, 250 eV) : (a) undamaged ; (b) 5×10^{14} ; (c) 1.5×10^{15} ; (d) 3×10^{15} ; (e) 7×10^{15} ; (f) 1.5×10^{16} ions/cm². Mod. $1 V_{p-p}$; 2 500 eV electrons.

of the saturation fluence. In addition, when decreasing the ion energy (Fig. 3), the SiO_x peak disappears later than the Si peak. Thus, the SiO_x is detectable at lower damage densities than the Si peak. Note that, even on undamaged SiO₂, a small SiO_x type inflection may be detected with improved resolution (modulation $1 V_{p-p}$ or less), which is the case in figure 2 and reference [3].

Further tendencies, like the increase of the damage saturation fluence and of the Si peak height with decreasing ion mass, have already been reported [1] and may be understood by a decreasing sputter rate and an increasing ion range.

Fig. 3. — Si LVV Auger spectra of ion bombarded SiO₂: evolution of SiO_x and Si peaks as a function of ion mass and ion energy (raw spectra: heights unnormalized to reference surface). Mo. 2 V_{p-p}; 2 500 eV electrons.

Finally, note that, whereas the Auger peak of implanted Ar (216 eV) is easily measured in ion-bombarded Si, it escapes detection in ion-bombarded SiO₂ (probably due to a larger penetration).

3.2 IONS IN THE LOW-ENERGY RANGE AROUND 100 eV. — Over the energy range investigated here and even beyond (up to 1.5 keV) Ar⁺ ions differ from Ne⁺ and He⁺ ions by the absence of the free Si peak. The only damage feature induced by Ar⁺ ions is the SiO_x peak which has a threshold at 100 (± 10 eV). In the case of Ne⁺, the SiO_x peak has its threshold at 75 (± 5 eV); for He⁺, the SiO_x peak is still large at 80 eV, which is the minimum energy we could achieve with this gas (Fig. 3).

Consider next the behaviour of the free Si yield as a function of ion energy, for the two species giving rise to a measurable free Si signal (Ne⁺, He⁺). The free Si yield, or dissociation yield, is defined as the ratio of the free Si peak height to the height of the SiO₂ peak of the reference surface [2]. There is a striking difference between Ne⁺ and He⁺ (Fig. 4). For Ne⁺, the yield decreases and vanishes around 80 eV. For He⁺, the yield starts rising below 250 eV and increases steadily up to 80 eV (limit of our measurements). A maximum would probably be attained for a few tens of eV.

Fig. 4. — Variation of free Si yield as a function of ion energy for Ne⁺ and He⁺.

4. Discussion.

The discussion is organized as follows. Firstly, we discuss the change in bonding representative of ion-induced damage, as compared to damage caused by the electron beam only or else by the combination of ion and electron bombardment. Next, we propose a semiquantitative evaluation of the composition of the altered layer and compare to calculations based on collisional sputtering. Then, we discuss the dependence of damage upon ion energy and ion mass, which raises questions about the mechanism of the interaction. Finally, we briefly comment upon the SiO₂-type sensitivity of the damage.

4.1 BONDING STATES IN THE ALTERED LAYER.

Ion-induced damage is characterized by two features: the SiO_x and the Si peaks, which coexist in various proportions (according to ion mass and ion energy). The SiO_x peak is attributed to a suboxide component, which is metastable and behaves similarly to vacuum-deposited SiO films [4]. For more details, see reference [1]. The Si peak is attributed to small clusters of elemental Si [1, 5, 6]. This picture of the ion-bombarded surface is in agreement with findings on other oxides [7], which show the coexistence of the initial oxide, the suboxide and the metal.

By contrast, electron bombardment alone does not generate the SiO_x feature [1, 2, 8]. Thus, although its detailed nature is not known, the SiO_x configuration appears connected with collisional sputtering and should belong to the class of vacancy-related centers. The Si component is generated as well by the lighter inert gas ions as by electrons [1, 2, 8]. Therefore, a participation of electronic sputtering (bond-breaking) is not excluded.

When electron bombardment follows ion bombardment (Fig. 1c), the dominant damage feature becomes the free Si peak (due to the metastability of the SiO_x component) [1, 2]. The SiO_x disproportionates into Si and SiO₂ [2]; this electron-induced rearrangement occurs at constant O content, i.e. the O deficiency is fixed by the ion bombardment. Turned differently, the ion-bombarded surface is stabilized against further O loss due to the electron beam.

The case of simultaneous ion and electron bombardment (which is of interest in Auger sputter profiling and in plasma treatments) is not feasible in our apparatus. Nevertheless, one can extrapolate and expect the resulting surface composition to depend on the ratio of electron to ion current density (i.e. of dissociation to sputter rate): when this ratio increases, the Si component should increase at the expense of the SiO_x component. This tendency is implicitly contained in reference [9], figure 7.

Considering the advantage of photoemission in terms of damage and ease of interpretation of the

fine structure, it would be interesting to investigate the Si 2p bonding states by surface-sensitive photoemission.

4.2 COMPOSITION OF THE ALTERED LAYER. — Auger peak intensities can be used to obtain semiquantitative information about the composition of the ion-damaged surface. From the measured attenuation of the O Auger peak, one can evaluate the O loss.

Suppose that the O deficit is concentrated in a thin surface layer of thickness $\lambda/2$, λ being the inelastic mean free path of the O Auger electrons in SiO₂ (about 10-15 Å) and that this thickness is independent of the ion penetration. This assumption is based on following arguments: a) the shallow depth of origin of sputtered particles [10, 11]; b) the localization of the dissociation in the first few atomic layers, thus escaping detection by the less surface-sensitive XPS probe [2]; c) the insensitivity of the dissociation yield to ion energy above 300 eV (Fig. 4).

From the exponential variation of Auger intensity as a function of depth D : $I/I_0 = \exp^{-}(D/\lambda)$, we calculate that 40 % of the Auger intensity originates from the top $\lambda/2$ thick layer. The Auger intensity is taken as proportional to the peak-to-peak height of the derivative peak. Calling $h_0(O)$ the O peak height of the reference surface, $h_d(O)$ the O peak height of the damaged surface and x the atomic ratio O/Si, we may write the proportionality of the number of O atoms in a slab of thickness $\lambda/2$ to the Auger intensity:

$$\frac{x}{2} = \frac{h_d(O) - h_0(O) \times 0.6}{h_0(O) - h_0(O) \times 0.6}$$

$0.6 h_0(O)$ representing the contribution from the undamaged substrate below the altered layer. Introducing the attenuation of the Auger intensity: $A = 1 - h_d/h_0$, we get: $x = 2(1 - A/0.4)$; the coefficient 0.4 is directly related to the assumed depth of the altered layer. The values of the calculated atomic ratios are given in table I.

Table I. — *Composition of damaged surface layer from AES.*

ion	A (%)	x	Composition
Ar ⁺	7	1.65	SiO _{1.65}
Ne ⁺	11	1.45	SiO _{1.45}
He ⁺	17	1.15	SiO _{1.15}

(A = attenuation of O Auger peak; x = atomic fraction O/Si).

It is worth checking whether the composition deduced from AES is compatible with that predicted by the preferential sputtering model.

We use the formula applicable to the oxide of a metal M [13]:

$$(X_O/X_M)_s = (X_O/X_M)_b \times (Y_M/Y_O)$$

which relates the surface (s) and bulk (b) atomic fractions X of the constituents to their sputtering yields Y .

The sputtering yields may be evaluated from [14]:

$$Y_M/Y_O = \alpha_M/\alpha_O \times \gamma_M/\gamma_O \times U_0(O)/U_0(M)$$

where α depends on the ratio of ion mass to target atom mass and may be found in reference [9], figure 3, γ is the usual kinematical factor and U_0 the surface binding energy. The U_0 's being less well-known quantities, we replace their ratio by a constant K .

Putting $M = \text{Si}$ and $(X_O/X_{\text{Si}})_b = 2$, the calculated atomic fraction in the altered layer is respectively: 1.36 K (Ar⁺), 1.29 K (Ne⁺) and 0.80 K (He⁺), which scales roughly with the experimental values (Tab. I), respectively: 1.65, 1.45 and 1.15.

Fitting calculated to experimental values, K can be estimated as: 0.6 (Ar⁺), 0.56 (Ne⁺) and 0.71 (He⁺), so that the mean value is close to: $K = U_0(O)/U_0(\text{Si}) = 2/3$. In a simple interpretation the surface binding energy is proportional to the number of bonds. This naive argument seems to work in the present case. Indeed, if one neglects low-binding energy species like non-bridging O, the surface undergoing sputtering would mainly contain trivalent Si and divalent (bridging) O.

To sum up, in the medium ion energy range, the composition of the surface layer, deduced from AES, agrees reasonably well with that predicted by collisional sputtering.

4.3 MECHANISMS. — The question of the mechanisms involved is raised by observations made as a function of ion mass in the low-energy range.

Consider first the behavior of the SiO_x peak. Damage thresholds occur in the region 75 (Ne⁺) to 100 eV (Ar⁺), which seems reasonable if the sputtering yield becomes negligible. Note that several authors, investigating the Ar⁺/SiO₂ system, measure sputtering yields down to 40 eV [15]. Hence, there should be an energy range, between 40-100 eV, within which SiO₂ may be sputtered by Ar⁺ ions without suffering any damage (at least as detected by AES).

Turning to the Si peak, we notice a fairly constant free Si yield in the medium energy range for both Ne⁺ and He⁺. However, at lower energies, there is a drastic difference between the two projectiles. In the former case, the yield decreases to zero as the

sputtering threshold is approached. In the latter case, the yield increases continuously when the energy is lowered in the range 80-250 eV (Fig. 4). This may be attributed to the intervention of a new process involving, either a different type of elastic collision, or inelastic collisions leading to electronic excitation of the Si-O bond followed by bond rupture. Both points of view may be found in the literature [16, 17], when trying to interpret the change of composition of oxides as a function of ion mass and energy.

Consider first elastic collisions. Two processes (in the case of normal incidence) may cause sputtering [18, 19]:

— type I: ejection by the projectile after its reflection on a subsurface atom;

— type II: ejection by one of the target atoms set in motion during the microcascade generated by the projectile. Several target atoms must be involved in order to reorientate the momentum outwards.

For Ne⁺ (mass comparable to target atoms), only process II needs to be considered; it becomes inefficient when the number of displaced atoms becomes too small.

For He⁺ (much lighter than target atoms), both processes are feasible. The change of slope observed near 200-250 eV (Fig. 4) may be assigned to a transition between type I and type II, the former predominating at lower energies. However, it is not clear why backscattered He would sputter O atoms much more efficiently than Si atoms, leading to the enhancement of the free Si component. Possibly, electronics effects play a part here by modifying the ratio of surface binding energies $U_0(\text{O})/U_0(\text{Si})$.

Indeed, a different interpretation may be sought, based on inelastic collisions involving ionization, electronic excitation [20]. The result may be, either bond rupture and desorption, or bond weakening, which means reduced surface binding energy, hence increased sputtering. In that regard, O atoms (electronegative species) would be more affected. In favor of this kind of explanation is the observation

that the free Si component can be produced as well by ions as by electrons (see 4.1) or even by photons [21], i.e. by ionizing radiation.

Among the various electronic effects, consider in particular Auger neutralization (AN) of the low energy inert gas ion, a process thoroughly investigated by Hagstrum [22] in the case of metals and semiconductors. The general trends for the Auger neutralization yield and for the free Si dissociation yield are similar. Both increase when the ion becomes lighter, which is related to the increase in ionization energy. Moreover, both yields increase when the ion energy is lowered in the range between several hundreds of eV and a few tens of eV.

Within the surface layer, AN represents a damaging event: the Si-O bond goes through an excited state containing two holes in the valence band, which means weakening or rupture of the bond.

Outside the surface, AN shows up by electron emission. Using the appropriate terminology, AN is a source of potential emission, as opposed to kinetic emission which predominates at higher energies. An ion velocity of about 1×10^7 cm/s is considered typical of the upper limit of the potential emission regime... For He⁺ ions, this is precisely the velocity, corresponding to an energy of 250 eV, near which a change of slope in the upper curve of figure 4 occurs.

4.4 COMMENTS ON SiO₂-TYPE SENSITIVITY OF THE DAMAGE. — The nature and the creation efficiency of bulk defects at higher energies (implantation range: tens to hundreds of keV) are known to depend markedly on the precise nature of the target: crystalline or vitreous [24], wet or dry oxide [25], etc.

A similar influence is expected for surface damage induced by low energy particles; e.g. preliminary work on a thick wet oxide shows considerably less radiation damage than with the present thin dry oxide. Therefore, the behavior of a particular type of SiO₂ sample should not be generalized without caution to other varieties (differing by their structure, processing, impurity content, etc.).

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