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Plasma etching to enhance the surface insulating stability of alumina for fusion applications

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ABSTRACT

A significant increase in the surface electrical conductivity of alumina, considered one of the most promising insulating materials for numerous applications in fusion devices, has been observed during ion bombardment in vacuum due to oxygen loss by preferential sputtering. Although this is expected to cause serious limitations to insulating components functionality, recent studies showed it is possible to restore the damaged lattice by oxygen reincorporation during thermal treatments in air. These studies also revealed a correlation between conductivity and ion beam induced luminescence, which is being used to monitor surface electrical conductivity degradation and help qualify the post irradiation recovery. Work now carried out for Wesgo alumina considers oxygen implantation and plasma etching as additional methods to improve recovered layer depth and quality. Both conductivity and luminescence results indicate the potential use of plasma etching not only for damage recovery, but also as a pre-treatment to enhance material stability during irradiation.

1. Introduction

Surface electrical degradation in oxide ceramics as a consequence of H and He ion bombardment (~keV) has been associated with oxygen loss due to preferential sputtering [1]. The relevance and potential danger to future fusion devices such as ITER and DEMO is related to the ionization of the residual gas and acceleration of the ions by local electric fields in the region of the insulators required in these devices. More recently, combined studies of electrical degradation and oxygen related luminescent centre formation (F and F^+ centres), and evolution as a function of He ion fluence allowed one to interpret material degradation as the product of progressive formation of new oxygen vacancies, vacancy aggregates, and finally aluminium colloids, enhanced by oxygen loss in the uppermost region caused by preferential sputtering during irradiation [2–3]. It was found that this type of degradation could be partially reversed and the electrical properties restored by thermal annealing in air, due to re-incorporation of oxygen into the surface region. However subsequent luminescence measurements indicated that the recovered layer thickness may still be insufficient in order to achieve enough stability under further irradiation and/or to withstand high voltages depending on the specific requirements.

Present work carried out in Wesgo AL995 initially aimed to overcome this limitation by selectively adding oxygen at the required depth by ion implantation. This technique is complex compared with thermal annealing, especially for application in areas of difficult access, and the results show that the efficiency of the "re-oxidation" process is limited by competing oxygen sputtering. In contrast experiments using low energy (≤1 keV) oxygen plasma etching have proved to be highly successful. Not only is the damaged area rapidly removed, with complete recovery of the surface electrical and luminescence properties, but also on re-irradiation the surface shows enhanced resistance to degradation. This marked improvement, possibly related to surface oxygen saturation, is now being considered as a potential pre-treatment to extend the service life of insulating components.

2. Experimental procedure

Polycrystalline Wesgo AL995 α-alumina samples (Morgan Matroc Ceramics) were used in the present study. Electrical degradation at the surface region was induced by 45 keV He^+ irradiation using a 60 kV ion implanter at typical fluxes of ~$4{\cdot}10^{12}$ ions/cm^{2}s and at room temperature. Both surface electrical conductivity and light emission from the sample (collected from a thickness of

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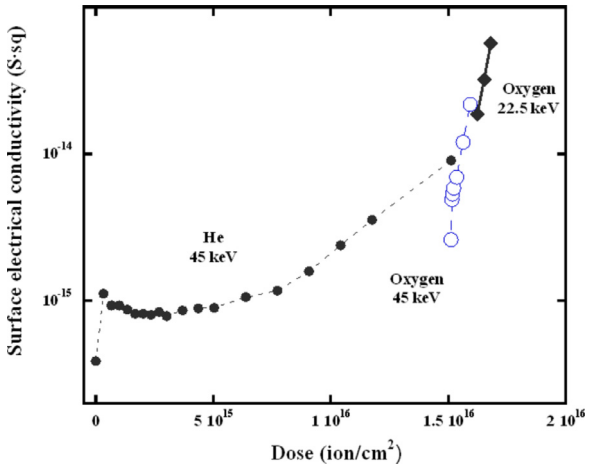

Fig. 1. Surface electrical conductivity as a function of He an O ion dose.

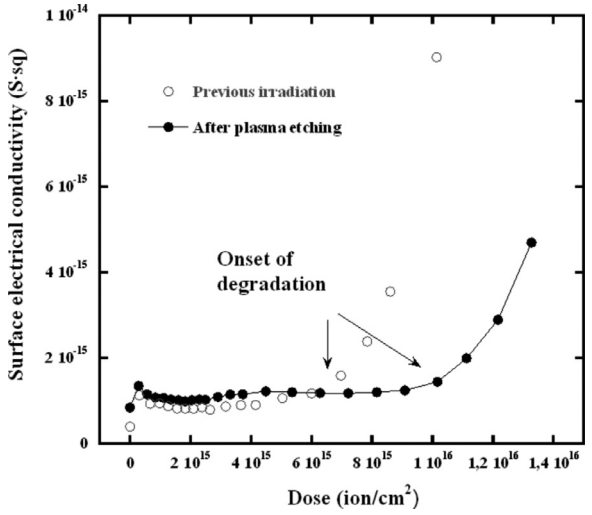

Fig. 2. Surface electrical conductivity as a function of He ion dose.

about ~160 nm depth according to ion penetration in alumina given by SRIM simulation) can be recorded in-situ making use of electrical and optical systems developed for this type of experiments as described elsewhere [3]. Oxygen implantation (45 and 22.5 keV) in previously damaged samples was carried out using the same experimental set-up, whereas a sputter coater (Edwards, S150B) operating at 1.3 kV in etching mode was employed for low energy oxygen implantation. The samples are mounted again in the ion implanter experimental line after each plasma etching treatment period so that surface electrical conductivity and IBIL can be measured after the recovery process on further irradiation.

3. Results

Results for oxygen implantation in Wesgo alumina are presented in Fig. 1. Surface electrical conductivity is plotted against irradiation dose for 45 keV He^+ ion bombardment (damage/reduction stage) followed by 45 keV and 22.5 keV oxygen implantation (recovery/oxidation stage), at a dose rates of $6{\cdot}10^{12}$ ions/cm^2s for helium and $0.5{\cdot}10^{12}$ and $2.5{\cdot}10^{12}$ ions/ cm^2s for 45 and 22.5 keV oxygen ions respectively, at room temperature.

As may be seen, surface electrical conductivity continuously increases during He irradiation above ~$5{\cdot}10^{15}$ ion/cm^2, after showing the typical initial behaviour (immediate rapid increase followed by a smooth decrease) [2–3].

Posterior oxygen implantation has been performed without removing the sample or altering vacuum conditions but after two hour time-lapse needed to change the source gas and stabilize the beam current. A clear conductivity recovery is observed after this delay, most probably due to interstitial-vacancy recombination at room temperature. However, renewed sputtering on the surface due to oxygen implantation produces further degradation in the material, even more rapidly than during the previous helium irradiation.

In contrast, a complete surface recovery was achieved when the sample was subjected to low energy oxygen ions (<1.3 keV) produced with a sputter coater. The system, operated at 1.3 kV and 30 mA, does not permit one to register conductivity data as a function of oxygen exposure, hence surface electrical current is given as a function of helium irradiation before and after a 25 minute plasma etching treatment (Fig. 2).

For the first irradiation with helium (open circles), performed at $6{\cdot}10^{12}$ ions/cm^2s at room temperature, conductivity degradation initiates above about $5{\cdot}10^{15}$ ions/cm^2. For the second irradiation (solid circles) after etching, performed under the same conditions, the initial conductivity not only has been fully recovered but also the sample shows improved performance under irradiation, with approximately double the dose needed for the onset of degradation.

Table 1
Sputtering yield in Al_2O_3 (SRIM).

Incident ion	Energy	at/ion (Al)	at/ion (O)	O/Al
Helium	45 keV	0.08	0.1	1.25
Oxygen	22.5 keV	2.05	2.71	1.32
Oxygen	45 keV	1.02	1.65	1.62

4. Discussion

Oxygen implantation at 22.5 and 45 keV causes additional damage in the sample surface with no recovery, the conductivity increase being even more severe than during helium irradiation (Fig. 1). These results may be directly related to the higher sputtering yield, according to SRIM [4] simulations given in Table 1. However, the use of low energy oxygen plasma etching seems to completely recover and even improve surface initial properties (Fig. 2).

Luminescence has proven to be a successful technique for the interpretation of degradation and recovery processes in aluminas. A reduction of about 60% of the maximum luminescence intensity reached by the F^+ centre is a precursor to the onset of the conductivity increase regardless of alumina material type [3–5]. Furthermore, the quality of the recovery after different treatments has been associated with the recovery of initial luminescence properties [6].

No indication of luminescence recovery has been observed for oxygen implantation. On the contrary, continuous reduction of IBIL takes place with oxygen dose, in agreement with the further material degradation revealed by the conductivity increase (Fig. 1). However, following plasma etching the spectrum recovers the initial structure (F, F^+, and Cr bands) lost during He irradiation and practically the same intensity (~70% F^+ band), as shown in Fig. 3.

These results represent a remarkable improvement when compared with earlier results obtained for thermal treatments in air:

From luminescence results (% of IBIL intensity recovered after annealing), a recovered layer thickness of about 13 nm was estimated for simple thermal annealing in air to about 300 °C in previously degraded Deranox alumina, this depth being increased to about 50 nm by annealing in an ionizing radiation field due to radiation enhanced diffusion [6].

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Table 2
IBIL and conductivity recovery.

	Alumina	Onset of degradation (ion/cm^2)		IBIL recovery*
		Before	After	
Annealing in air	Deranox 995	$1.3{\cdot}10^{16}$	$3{\cdot}10^{14}$	10%
Annealing in air + irradiation	Deranox 995	$1{\cdot}10^{16}$	$7{\cdot}10^{15}$	30%
Plasma etching	Wesgo 995	$6{\cdot}10^{15}$	$1{\cdot}10^{16}$	80%

* IBIL intensity after treatment relative to "as received"

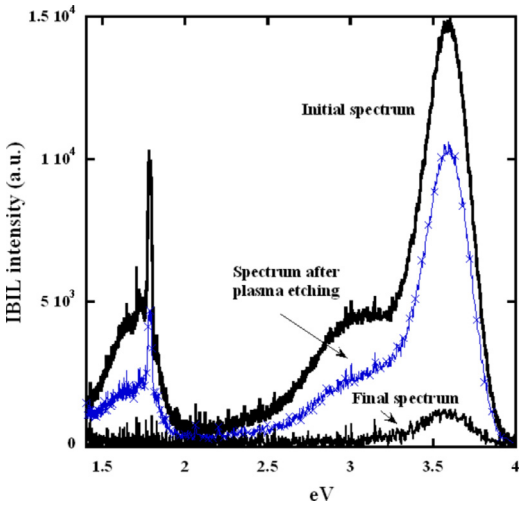

Fig. 3. Luminescence spectra induced by He irradiation before plasma etching (initial and final spectra after 10^{16} ion/cm^2), and after oxygen plasma etching treatment.

Although initial surface electrical conductivity is fully recovered in all cases, it must be taken into account that although surface electrical conductivity is measured in a very shallow region, luminescence is collected from a volume of about ~160 nm in depth corresponding to the 45 keV He ion penetration in alumina given by SRIM simulation (damaged volume), and is therefore a good indicator of the real state of the material. In fact, the material stability under further irradiation presents important differences depending on the luminescence recovery, being improved for annealing during exposure to ionizing radiation [6] and more notably for plasma etching (Fig. 3).

Table 2 compares the irradiation dose at which electrical conductivity begins to increase for samples "as received" and "recovered" by different methods with the grade of luminescence recovery. While for small IBIL recoveries (10–30%) on re-irradiation the onset of degradation takes place at lower dose than for the "as received" samples indicating incomplete recovery, but in the case of the plasma etching the degradation is even delayed.

IBIL recovers to ~10% of the initial (as received) intensity for annealing in air, and ~30% for annealing in air during irradiation. However, for plasma etching the F^+ band reaches ~70% of the initial intensity. This implies a recovered material layer (oxygen penetration) of about 110 nm (70% of 160 nm, total irradiated thickness). SRIM calculations give a maximum penetration in the order of few nm for the < 1 keV oxygen beam, comparable to the aluminium oxide layer formed in air at moderate temperatures. The higher than expected recovery is most probably due to the material elimination during the high sputtering rate in the etching process rather than re-oxidation.

Examination of the whole IBIL spectrum from 1 to 4 eV reveals that there are important differences between the heating methods and the plasma etching technique.

Fig. 4(a, b) shows initial luminescence spectra taken at room temperature for Deranox alumina before and after the annealing treatments discussed above [6]. An additional band for annealed samples (more intense when annealing during irradiation) is observed at 1.5 eV, which might be related to F_2 centres [7], or impurity segregation. This is indicative of active processes that are taking place as a consequence of heating, enhanced by ionization. No indication of this new band is observed in this region for Wesgo, as is clearly seen in Fig. 4c despite the difficulties introduced by the additional band overlapping the Cr^{3+} emission (associated with Fe [8–9]). The identical luminescence structure suggests a physical removal of the damaged layer (surface cleaning).

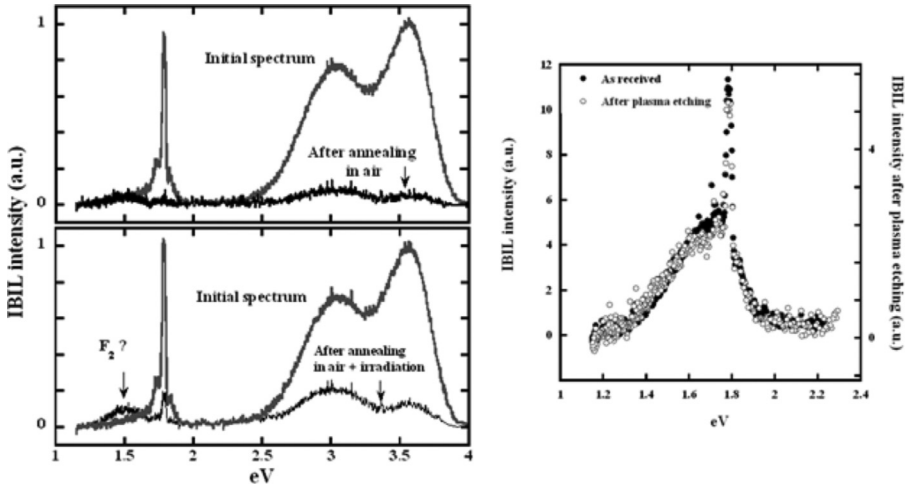

Fig. 4. IBIL spectra for an "as received" Deranox sample and after 10^{16} ion/cm^2 He irradiation plus posterior annealing in air (a), and posterior annealing in air during electron irradiation (b). IBIL spectra (detail) for Wesgo "as received", and after 10^{16} ion/cm^2 He irradiation plus posterior plasma etching treatment (c).

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5. Conclusions

Surface electrical conductivity and He^+ ion induced luminescence data for Wesgo alumina have been obtained before and after different treatments involving oxygen. The results indicate that oxygen implantation produces extra damage in the surface region, while plasma etching is an efficient method to remove the damaged layers without producing any additional deterioration in the remaining surface beneath.

The quality of the recovery, measured not only for surface electrical conductivity but also luminescence intensity, compared with that previously reported after thermal treatments up to 300 °C is far superior for plasma etching technique.

In addition, the superior behaviour under further irradiation after this process suggest the potential use of this method not only for damage recovery, but also as a pre-treatment to enhance material stability during irradiation, and is currently being investigated using different plasma parameters and materials.

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