Krug *et al.* Reply: In a Comment [1] on our recent Letter [2], Copel discusses features in our XPS data that had not been explained, presents new XPS and MEIS data, and questions the validity of the diffusion-reaction model that we proposed.

The first point raised by Copel is the origin of the Si $2p$ photoelectron peak at 98.5 eV binding energy appearing in the analysis of Al_2O_3 films on Si(001) after annealing in O_2 at 800 °C for 30 s, which was unclear in our Letter [2]. Thickness inhomogeneities [1] should indeed be the reason for the above-mentioned peak, which is absent from Copel's results as well as from our results for annealing at lower temperatures. Film inhomogeneities could be induced by extrinsic impurities, as suggested by Copel, or avoided by annealing in ultrahigh vacuum prior to oxidation, as performed by Copel [1]. Such annealings [3] densify the films, reduce oxygen diffusivity during subsequent oxidation, and may result in the observed enhanced stability. In this case, it would be Copel's merit to have found optimal preoxidation annealing conditions.

Given the presence of film inhomogeneities in the sample oxidized at 800 °C in our work, the assumptions underlying our diffusion-reaction model are questioned [1]. On the contrary, we understand that by detecting Si migration and fixation in the Al_2O_3 film in essentially thickness inhomogeneity-free conditions, Copel provided an important confirmation of our model adequacy. In fact, without oxygen diffusion and reaction one cannot explain Si migration, partial replacement of Al by Si, and Al loss (not entirely quantified in [1]). Furthermore, the specific criticism addressed in the last sentence of the Comment [1] concerning oxygen removal from Al_2O_3 by excess Si can also be justified. An estimate of the coefficients in the model equations from experimental data is required in order to quantify the relative contributions of different diffusion and reaction processes. Since this information is not yet available, we used the simplest assumption of reactions yielding stoichiometric compounds according to thermodynamic stability data, which is not necessarily valid. Unfortunately, due to partial superposition of Al and Si signals, the MEIS technique used by Copel did not add the necessary information in this sense.

An additional, important issue [4] not addressed by us or by Copel regards oxygen diffusion from the gas phase to the Al_2O_3-SiO_2/Si interface. This constitutes a basic assumption of the model, as oxygen is taken to trigger Si diffusion and subsequent reaction in the Al_2O_3 network. In order to investigate oxygen transport, we annealed Al_2O_3 films on Si(001) in $^{18}O_2$ for various times at 700 °C, a temperature at which we observed Si migration and fixation without any effect attributable to thickness inhomogeneities. Much thicker (36 nm) films were deposited and oxidized as before [2], aiming at privileging information from the surface and bulk of the films, without contribution of solid-solid interfaces. Excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction around the narrow and isolated resonance at 151 keV [5] are shown in Fig. 1. Experimental data (open symbols) can be unambiguously simulated (solid lines) assuming complementary error function-like ^{18}O profiles (see inset) whose widths increase with increasing annealing time. Thus, far from solid-solid interfaces the profiles correspond (see Appendix B of [5]) to a mechanism whereby ^{18}O diffuses by a vacancy or an interstitialcy mechanism, replacing O atoms in the Al_2O_3 network which can diffuse. This diffusive transport of oxygen from the gas phase across Al_2O_3 films on Si(001) implies a constant supply to the oxide/Si interface, as assumed in our model.

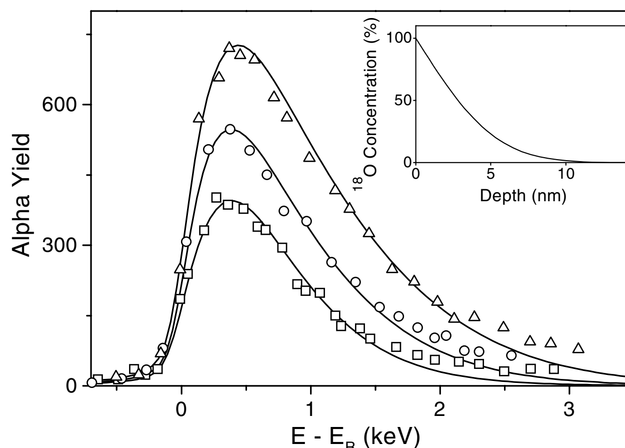

FIG. 1. Experimental (symbols) and simulated (lines) excitation curves of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction for 36 nm thick Al_2O_3 films on Si(001) annealed in $^{18}O_2$ at 700 °C for 90 (squares), 120 (circles), and 180 s (triangles). The ^{18}O profile assumed for the simulation of data from the sample annealed for 180 s is shown in the inset, where 100% corresponds to the concentration of O in Al_2O_3.

C. Krug,[1] E. B. O. da Rosa,[1] R. M. C. de Almeida,[1] J. Morais,[1] I. J. R. Baumvol,[1] T. D. M. Salgado,[2] and F. C. Stedile[2]

[1]Instituto de Física, UFRGS
Avenida Bento Gonçalves, 9500
Porto Alegre, RS, Brazil 91509-900

[2]Instituto de Química, UFRGS
Avenida Bento Gonçalves, 9500
Porto Alegre, RS, Brazil 91509-900

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