Microdefects in Al 2 O 3 films and interfaces revealed by positron lifetime spectroscopy

Jun Xu, B. Somieski, L. D. Hulett, B. A. Pint, P. F. Tortorelli, R. Suzuki, and T. Ohdaira

Citation: Applied Physics Letters **71**, 3165 (1997); doi: 10.1063/1.120278
View online: http://dx.doi.org/10.1063/1.120278
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/71/21?ver=pdfcov
Published by the AIP Publishing

Microdefects in Al_2O_3 films and interfaces revealed by positron lifetime spectroscopy

Jun Xu,[a] B. Somieski, L. D. Hulett, B. A. Pint, and P. F. Tortorelli
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6142

R. Suzuki and T. Ohdaira
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

(Received 21 July 1997; accepted for publication 26 September 1997)

We have studied microdefects and interfaces of Al_2O_3 films on iron and nickel aluminide substrates using variable-energy positron lifetime spectroscopy. Di-vacancies, vacancy clusters, and microvoids were observed in the oxide scales. Their sizes and distributions were determined by the nature of the process used to synthesize the alumina film, and influenced by the composition of the alloy substrates. For oxide–iron aluminide interfaces, positron lifetimes are longer than those for the alumina layer itself, suggesting a greater defect concentration at such sites. © *1997 American Institute of Physics.* [S0003-6951(97)02547-3]

Surface oxides are used for various applications that range from thin films for microelectronics to thick ones that act as protective coatings for alloys and ceramics. Alumina is of particular interest for thick-scale protective layers because it is relatively inert and diffusion-protective. Understanding the nature of microdefects in oxide layers and at their interfaces is important, since these defects can significantly influence their adherence and ability to act as protective surface coatings.[1,2] Conventional methods for probing these defects include scanning and transmission microscopy (SEM and TEM),[3] which are sensitive to larger-scale (>a few nm) voids. For detecting smaller defects, which may be the precursor of larger voids,[4] positron spectroscopy is useful.[5,6] To date, no studies of alumina films using positron techniques have been reported. In this letter, we present positron lifetime studies of alumina films with various positron energies in the range necessary to enter the alumina scales and reach their interfaces with metals.

Alumina layers were synthesized by two different processes: (1) oxidation of iron– and nickel–aluminide substrates for 2 hr at 1200 °C in flowing O_2 and (2) physical vapor deposition (PVD) on iron aluminide.[7] The thermally grown scales were prepared on both (69.9 at %)Fe-(28)Al-(2)Cr-(0.1)Y_2O_3 (referred to as $Fe_3Al+Y_2O_3$) and (48.95 at %)Ni-(51)Al-(0.05)Hf (referred to as β-NiAl+Hf) substrates, which were polished to 0.3 μm and cleaned ultrasonically in acetone and methanol baths prior to oxidation. These two substrates were chosen because β-NiAl+Hf has a relatively void-free metal–oxide interface while $Fe_3Al+Y_2O_3$ forms large interfacial voids.[8] These films have a crystalline structure (α) with a thickness of about 1 μm. The alumina film deposited on (66.9 at %)Fe-(28)Al-(5)Cr-(0.1)Zr (referred to as Fe_3Al+Zr) by PVD was amorphous and approximately 5 μm thick. While the PVD Al_2O_3 is relatively pure, there is ~0.5 wt % Fe or Ni in the thermally grown α-Al_2O_3 scales on iron– and nickel–aluminides, respectively.

Positron lifetime measurements were conducted in a high-vacuum chamber (10^{-8} Torr) which is attached to the positron beam line at the Electrotechnical Laboratory. Detailed descriptions of the positron apparatus appeared in Ref. 9. Positrons were produced by converting gamma rays, generated by bombardment of 75 MeV linac electrons on a tantalum target, into electron–positron pairs and then moderated in tungsten plates. The positron pulses are stretched in a Penning trap and rebunched with a high frequency (178 MHz) and narrow width (<300 ps). The positron energy was varied in the range of 0.25–23 keV by biasing the sample.

Figure 1 shows the positron lifetime spectra for the thermally grown Al_2O_3 scales on both $Fe_3Al+Y_2O_3$ and β-NiAl +Hf and for the PVD Al_2O_3 film on Fe_3Al+Zr. The incident positron energies were 5 keV, corresponding to a mean im-

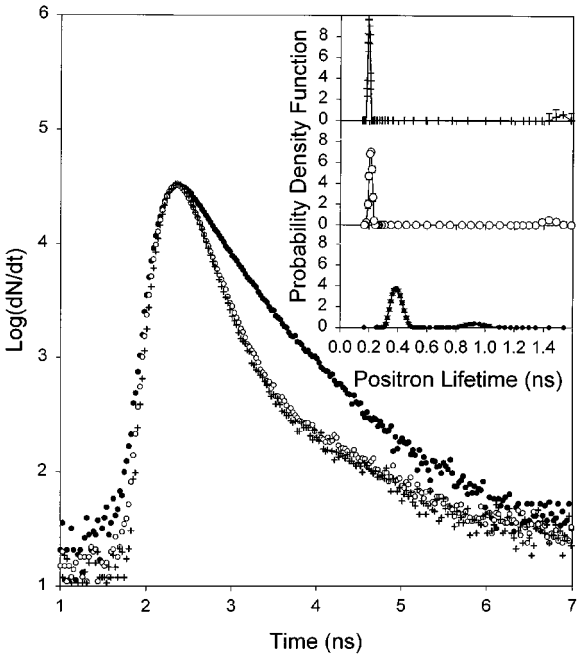

FIG. 1. Semi-log plots of the counting rates as functions of the arrival time of annihilation gamma rays for the thermally grown Al_2O_3 scales on both $Fe_3Al+Y_2O_3$ (open circles) and β-NiAl+Hf (crosses), and for the PVD Al_2O_3 film on Fe_3Al+Zr (filled circles). Inset: Probability density functions as a function of positron lifetime, resulting from Laplace inversion (CONTIN).

[a]Electronic mail: xuj2@ornl.gov

plantation depth of ~0.13 μm.[10] The positron lifetime spectra were analyzed by Laplace inversion (CONTIN)[11] which deconvolutes the time spectra into the probability density function (pdf) as a function of positron lifetime, as shown in the insert. Total counts of the spectra are limited to be around 5×10^5, which may affect the width in the pdf peaks.[12] However, the peak positions are reasonably accurate since they are generally not altered by statistics. For the α-Al_2O_3 scales on $Fe_3Al+Y_2O_3$ and β-NiAl+Hf, the majority of positrons annihilate around 206 and 194 ps, respectively, with satellite peaks (4%) of about 1400–1500 ps.

Positron lifetimes in defect-free alumina lattices are about 140 ps and positrons trapped in aluminum-site vacancies in alumina have lifetimes of about 165 ps.[13] Thus, the lifetimes (194–220 ps) measured for the scales are estimated due to mainly di-vacancy sites by a linear extension of the above two lifetimes, as indicated in Ref. 14 for semiconductors. Laplace inversion also reveals that the positron lifetimes are significantly different for the Al_2O_3 scales on $Fe_3Al+Y_2O_3$ (206 ps) and β-NiAl+Hf (194 ps) even though they were formed by the same oxidation process. This lifetime difference may be due to the chemical composition of the scales, particularly the iron and nickel cation impurities.

For the PVD film, the main component of the lifetimes is around 388 ps, much longer than the lifetimes for the thermally grown scales. The PVD-film lifetime may be due to the larger interatomic spaces in the amorphous structure, which are approximately equivalent to the size of a cluster of about 8 atomic vacancies in the crystalline mode.

Voids are also indicated by appearance of the long lifetime components around 600–1400 ps. TEM images indicate that the thermally grown Al_2O_3 scales contain a few percent voids, generally 20–100 nm in size.[2] This would yield a long positron lifetime (>5 ns) if positronium is formed in these voids. The observed shorter lifetimes may indicate that positrons are attached to the inner wall of the voids or that the voids that trap positrons are much smaller.

Positron lifetime spectra measured as a function of positron energy in the range 0.25–23 keV, provided depth profiles of defects in the scales on $Fe_3Al+Y_2O_3$. Figures 2(a) and 2(b) show the positron lifetimes and their intensities, respectively, as functions of positron energy. τ_2 represents the surface lifetime. τ_1 and τ_3 are the short and long components of the bulk lifetime, respectively. The intensity of the surface component (I_2) decreases as the energy increases, while the intensity of the bulk component (I_1) varies inversely. This variation is interpreted with the positron diffusion process in which the low-energy positrons diffuse back to the surface, while the high-energy positrons are trapped in the bulk. The diffusion length was estimated to be about 20 nm, which is much shorter than that of perfect alumina lattices (100 nm). The truncated length confirms the high concentration of microdefects in the scales.

A clear difference was observed between the lifetime spectra of 15 and 20 keV positrons injected into the alumina scale on $Fe_3Al+Y_2O_3$, as shown in Fig. 3. Laplace inversion reveals that the lifetime for 15 keV peaks around 205 ps, while 20 keV positrons annihilate around 219 ps. This difference is believed to be due to the interface since the mean depth of positron penetration for 20 keV is close to the 1 μm

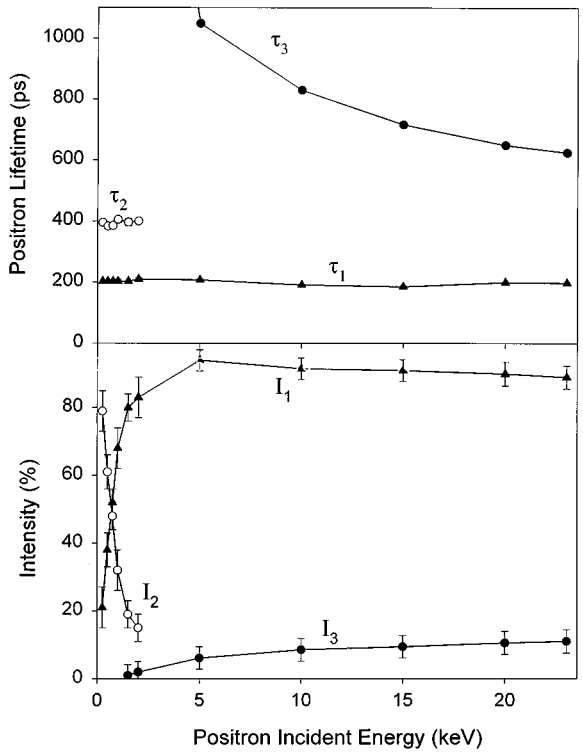

FIG. 2. (a) Positron lifetimes and (b) related intensities for thermally grown alumina scale on iron aluminide substrate as a function of positron energy. For lower energies (<2 keV), I_2, I_2, I_3, τ_2 and τ_3 were determined by fitting (POSFIT) with τ_1 fixed at the average bulk lifetime (202.5 ps). For other energies, all parameters were obtained by fitting.

scale thickness. Possible causes of increase are as follows: (1) interfacial dislocations, (2) larger vacancy clusters, and (3) the chemical difference around the interface. The difference between the positron lifetimes for 15 and 20 keV positrons injected into alumina scales on β-NiAl+Hf is not as large as that observed for $Fe_3Al+Y_2O_3$. This suggests that the size of the interfacial vacancy clusters for nickel alu-

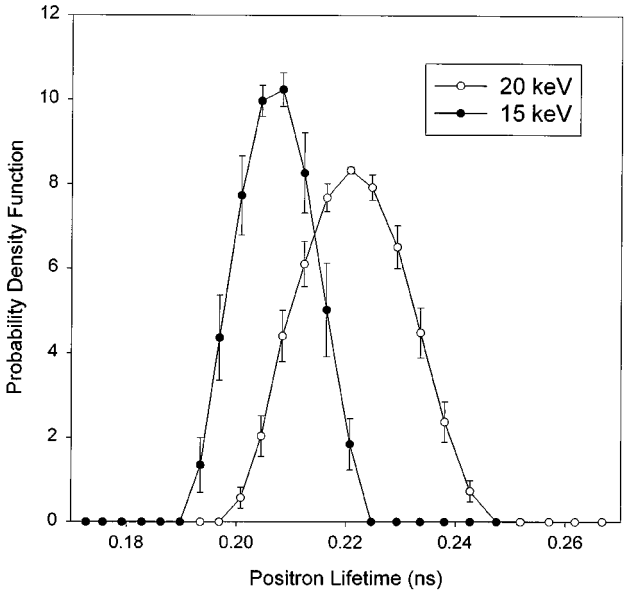

FIG. 3. Probability density functions as a function of positron lifetime for 15 and 20 keV positrons ejected into the thermally grown Al_2O_3 scale on the iron–aluminide substrate.

minide is not as large as that for the iron aluminide–alumina interface. This correlates with the larger number of voids at the oxide–metal interface for $Fe_3Al+Y_2O_3$ than for β-NiAl+Hf.[8]

In summary, for the first time, microdefects in Al_2O_3 films and Al_2O_3-metal interfaces have been evaluated using a positron probe. Di-vacancies, vacancy clusters, and voids were found in the alumina films, which varied significantly between deposited amorphous Al_2O_3 and thermally grown α-Al_2O_3 and were affected by the type of substrate. For the thermally grown α-Al_2O_3, the vacancy cluster size at the Al_2O_3-Fe_3Al interface is larger than in the bulk of the film; although this is not apparent for the film grown on nickel aluminide.

Research is sponsored by Division of Materials Science of DOE under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. The authors acknowledge the support from Science Technology Agency of Japan and Ion Brown at LBL for making the PVD coating. BAP was supported by DOE Distinguished Postdoctoral Research Program administrated by ORISE.

[1] J. Smialek and R. Gibala, *High Temperature Correlation*, edited by R. Rapp (NACE, Houston, TX, 1983), p. 76.
[2] B. A. Pint, Oxidation Metals **48**, 303 (1997).
[3] M. J. Bennett and G. W. Lorimer (editors), *Microscopy of Oxidation* (London, 1991).
[4] P. Hancok and J. R. Nicholls, Mater. Sci. Technol. **4**, 398 (1988).
[5] R. Suzuki, T. Mikado, H. Ohgaki, M. Chiwaki, T. Yamazaki, and Y. Kobayashi, Phys. Rev. B **49**, 17 484 (1994).
[6] P. Willutzki, J. Stomer, G. Kogel, P. Sperr, D. T. Britton, R. Steindle, and W. Triftshauser, Mater. Sci. Technol. **5**, 548 (1994).
[7] I. G. Brown and Z. Wang, in *Proceedings of the Ninth Annual Conference on Fossil Energy Materials*, edited by N. C. Cole and R. R. Judkins, U.S. DOE, August, 1995, pp. 239–246.
[8] B. A. Pint, P. F. Tortorelli, and I. G. Wright, Werst. Korros **47**, 663 (1996); B. A. Pint, I. G. Wright, W. Y. Lee, Y. Zhang, K. Prubner, and K. B. Alexander, Mater. Sci. Eng. (1998) (in press).
[9] R. Suzuki, Y. Kobayashi, T. Mikado, H. Ohgaki, M. Chiwaki, and T. Yamazaki, *AIP Conf. Proc. 303*, edited by E. Ottewitte and A. H. Weiss (AIP, New York, 1994), p. 526.
[10] A. Vehanen, K. Saarinen, P. Hautojarvi, and H. Huomo, Phys. Rev. B **35**, 4606 (1987).
[11] R. B. Gregory, NIM **A302**, 496 (1991).
[12] Y. C. Jean and G. H. Dai, Nucl. Instrum. Methods Phys. Res. B **99**, 357 (1995).
[13] M. Forster, W. Claudy, H. Hermes, M. Koch, K. Maier, J. Major, H. Stoll, and H.-E. Schaefer, Mater. Sci. Forum **105–110**, 1005 (1992).
[14] M. J. Puska, *Positron Annihilation*, edited by L. Dorikens–Vanpraet, M. Dorikens, and D. Segers (World Scientific, New Jersey, 1988), p. 101.