Positron annihilation studies of the AlOx/SiO2/Si interface in solar cell structures
C. J. Edwardson, P. G. Coleman, T.-T. A. Li, A. Cuevas, and S. Ruffell

Citation: J. Appl. Phys. 111, 053515 (2012); doi: 10.1063/1.3691895
View online: http://dx.doi.org/10.1063/1.3691895
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v111/i5
Published by the American Institute of Physics.

Related Articles
Overcoming the bandgap limitation on solar cell materials
Energy transfer in CaYAlO4: Ce3+, Pr3+ for sensitization of quantum-cutting with the Pr3+-Yb3+ couple
GaAs/GaInNAs quantum well and superlattice solar cell
Understanding the operation of quantum dot intermediate band solar cells
Improved performance of multilayer InAs/GaAs quantum-dot solar cells using a high-growth-temperature GaAs spacer layer

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors
Positron annihilation studies of the AlO$_x$/SiO$_2$/Si interface in solar cell structures

C. J. Edwardson,$^{1,*}$ P. G. Coleman,$^1$ T.-T. A. Li,$^2$ A. Cuevas,$^2$ and S. Ruffell$^3$

$^1$Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom
$^2$College of Engineering and Computer Science, The Australian National University, Canberra, ACT 0200, Australia
$^3$Research School of Physics and Engineering, The Australian National University, Canberra, ACT 0200, Australia

(Received 4 October 2011; accepted 5 February 2012; published online 7 March 2012)

Film and film/substrate interface characteristics of 30 and 60 nm-thick AlO$_x$ films grown on Si substrates by thermal atomic layer deposition (ALD), and 30 nm-thick AlO$_x$ films by sputtering, have been probed using variable-energy positron annihilation spectroscopy (VEPAS) and Doppler-broadened spectra ratio curves. All samples were found to have an interface which traps positrons, with annealing increasing this trapping response, regardless of growth method. Thermal ALD creates an AlO$_x$/SiO$_x$/Si interface with positron trapping and annihilation occurring in the Si side of the SiO$_x$/Si boundary. An induced positive charge in the Si next to the interface reduces diffusion into the oxides and increases annihilation in the Si. In this region there is a divacancy-type response (20 ± 2%) before annealing which is increased to 47 ± 2% after annealing. Sputtering seems to not produce samples with this same electrostatic shielding; instead, positron trapping occurs directly in the SiO$_x$ interface in the as-deposited sample, and the positron response to it increases after annealing as an SiO$_2$ layer is formed. Annealing the film has the effect of lowering the film oxygen response in all film types. Compared to other structural characterization techniques, VEPAS shows larger sensitivity to differences in film preparation method and between as-deposited and annealed samples. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3691895]

I. INTRODUCTION

Surface recombination in crystalline Si (c-Si) solar cells has a high impact on efficiency.$^1$ Aluminum oxide (AlO$_x$) films have been found to provide excellent surface passivation.$^2$ However, neither the AlO$_x$/Si interface properties nor the charge trapping mechanism in the dielectric films are fully understood.$^3$ It has been found that the surface passivation mechanism of sputtered AlO$_x$ films is the same for those deposited by other methods. It is not the bulk of the AlO$_x$ film, or the O/Al ratio, that passivates but the formation of a silicon oxide (SiO$_2$) layer at the interface during annealing.$^4$ In this work we report the results of an investigation of the AlO$_x$/Si interface and the effect of different growth methods, film thickness and annealing using variable-energy positron annihilation spectroscopy (VEPAS) and Doppler-broadened spectra ratio curves. Positrons are an ideal probe due to high sensitivity to interfaces enabling defect and chemical analysis of this region.$^5$–$^7$

II. EXPERIMENTAL PROCEDURE

AlO$_x$ was deposited on 0.8 Ω · cm FZ p-Si using two different methods. The first was thermal atomic layer deposition (ALD),$^8$ used to grow 30 or 60 nm-thick films. Samples were deposited using a Cambridge Nanotech thermal ALD reactor. A cycle in the reactor consisted of a 15 ms injection of Al(CH$_3$)$_3$ vapor followed by a 5 s N$_2$ purge. The oxidation step consisted of a 15 ms injection of H$_2$O vapor followed by a 5 s purge with N$_2$ resulting in a deposition rate of 1.06 Å/cycle (0.6 nm/min). The second method was RF magnetron sputtering,$^4$ used to grow 30 nm-thick films. Material from an Al target was deposited onto a rotating silicon substrate (40 rpm) at 25 °C for ~5 min. The sputtering gases used were Ar (20 sccm) and O$_2$ (2 sccm) in a working pressure of 3 mTorr (<7 × 10$^{-7}$ Torr base pressure). RF power was 300 W (~130 V). A Maxtek TM-350 quartz crystal thickness monitor was used to measure a rate of deposition of 4.3 nm/min. Thicker (740 nm) sputtered films were also deposited on 0.8 Ω · cm FZ p-Si and 1 Ω · cm Cz n-Si. All samples were studied in the as-deposited state and after annealing at 425 °C in N$_2$ for 30 min.

The VEPAS technique implants positrons into a sample with energies $E$ between 0.25 and 30 keV. The energy dictates the positron implantation profile so the average response varies from the surface to ~4 μm. Once implanted the positrons rapidly thermalize and diffuse to either annihilate free electrons or become trapped in vacancy-type defects and interfaces. Annihilation occurs via the creation of two approximately anti-collinear 511 keV γ-rays. Due to the momenta of the annihilated electrons the 511 keV line is broadened; this broadening is measured using a high-purity Ge detector and characterized using the parameters $S$ and $W$, defined as the fractions of the annihilation line ($|511-E_C| \leq 4.7$ keV) in the central ($|511-E_C| \leq 0.85$ keV) and outer (2.2 \leq |511-E_C| \leq 4.7$ keV) regions, respectively. Individually

---

*aAuthor to whom correspondence should be addressed. Electronic mail: c.j.edwardson@bath.ac.uk.
these parameters are a measure of the average electronic momentum at the annihilation site, including vacancy-type defects, in which diffusing positrons are efficiently trapped. Analysis of $S(E)$, $W(E)$ can provide depth-dependent information and plots of $S$ versus $W$ can be used to examine individual annihilation states within the material. More details about the technique can be found in Refs. 9 and 10. VEPFIT (Ref. 11) is a fitting program which takes the raw $S(E)$ or $W(E)$ data and solves the positron diffusion equation to calculate annihilation parameters, effective positron diffusion lengths and electric fields in layers within each sample.

In the ratio curve technique the annihilation line, or spectrum peaked at 511 keV, is measured with high precision with a single Ge detector and further information is extracted from the higher momentum components contained in its wings. Core electrons have a characteristic momentum associated with the atom; this enables chemical analysis of the species that surround the annihilation site. Positrons are implanted at a single energy where the response is the greatest for the region of interest, e.g., the film or interface. The spectrum, collected typically for $\sim 48\ h$, is normalized to an area of $1.5 \times 10^7$ counts between 491 and 531 keV and divided by a reference spectrum, normally c-Si or c-Al whose defect concentration is lower than that detectable by positrons, to reveal any differences in the high momentum content between 511 and 531 keV. Haaks et al., also measured spectra using a single Ge detector and subtracted background as their peak-to-background ratio was $\sim 10^2$. For this experiment the peak-to-background ratio was $\sim 3 \times 10^3$ due to distancing and shielding of the source from the detector. While background was not subtracted, it should also be noted that (a) all spectra, including reference spectra, were taken specifically for the purpose of this study and (b) the structure in spectrum ratios here occur at gamma energies at which signal significantly exceeds the background.

III. RESULTS AND DISCUSSION

A. 30 and 60 nm thermal ALD films

Differences were investigated between the four thermal ALD samples - 30 or 60 nm AlOx films on 0.8 $\Omega \cdot$ cm FZ pSi - before and after annealing at 425 $^\circ$C in N2 for 30 min. Figure 1 shows $S(E)$ results for these samples. The $S$ parameter is normalized to unity for the bulk material. The mean positron implantation depth ($z$) is also shown where $z \approx (40/\rho)E^{1.6}$, where $\rho$ is the density of the material in g cm$^{-3}$. A response to the film can be seen in the 60 nm film samples as an inflection in the $S(E)$ curve at around 1.5 keV. This response is not as clear in the 30 nm film samples. All four plots show a rapid rise in the $S$ parameter until $\sim 6$ keV, an indication that the effective positron diffusion length ($L$) is quite short ($L \sim 10$ nm from VEPFIT) in this region. VEPFIT also finds that positrons are being efficiently trapped, i.e., $L \sim 0$ nm, in the AlOx/Si interface ($\sim 1$ nm) and are allowed to freely diffuse in the Si, i.e., $L \sim 250$ nm. Before annealing, this trapping interface has an $S$ parameter very close to that of bulk Si. The interface $S$ parameters of both samples, found by VEPFIT, rise to $\sim 1.01$ after annealing; to have this kind of response positrons must be annihilating on the Si side of the AlOx/Si interface, because the oxide – and vacancy defects in the oxide – have characteristic $S$ parameters which are significantly lower than bulk Si. This is feasible as it has been shown that there is a high negative charge density in the AlOx within $\sim 1$ nm of the interface created by a high oxygen-to-aluminum ratio from the incomplete ALD process during the first deposition cycles. Furthermore, this negative charge significantly increases following the low temperature annealing, usually by a factor of 100. A high negative fixed charge density strongly reduces the electron concentration, thus inducing a positive charge on the Si side of the thin insulating SiOx layer formed during the first ALD cycles. It is proposed that this positive charge stops the positrons from diffusing back into the AlOx and SiOx so that annihilation occurs in the Si at the SiOx/Si boundary.

Ratio curves were used to investigate further the defects within the two regions of interest here – the AlOx film and the interface – by collecting spectra at $E = 1.5$ keV and 6 keV, respectively.

Figure 2 shows the results at $E = 1.5$ keV for the 60 nm film samples, which were used because of the larger positron response to the AlOx film. The sample spectra are divided by a reference spectrum, in this case that for Cz Si, and plotted against gamma energies from 511 keV. The peak at $\sim 514.6$ keV in these samples is caused by the presence of oxygen. Using the absolute peak heights, there appears to be $\sim 9 \pm 2\%$ less oxygen response after annealing. Open

![FIG. 1. (Color online) Normalized $S(E)$ plot for AlOx films deposited by thermal ALD before and after annealing at 425 $^\circ$C in N2 for 30 min. Left: 30 nm film. Right: 60 nm film.](http://jap.aip.org/about/rights_and_permissions)
volume defects in the AlOₓ film may be being annealed away, reducing the likelihood of positrons trapping next to oxygen atoms, but oxygen may also be diffusing out of the film. Other studies³,⁴ have shown that annealing causes the growth of an SiO₂ interface, consistent with oxygen out-diffusion from the AlOₓ film. Figure 3 shows the ratio curve results using \( E = 6 \) keV. The 30 nm film samples were used because their \( S(E) \) response is dominated by the interface. Small oxygen peaks are present here not because there is oxygen present in the interface but because of the small overlap of the positron implantation profile with the surface/film. The dip in the ratio curves is believed to be a response to \( V_2 \) as vacancies result in a reduction of high-momentum content.¹⁹ To confirm this a sample of Si was implanted with 160 keV Ge to a fluence of \( 5 \times 10^{15} \) cm². A saturated \( V_2 \) type defect response was observed in \( S(E) \) at 6 keV; similar results were seen in Ref. 20. A line shape was thus taken at 6 keV and the resulting \( V_2 \) ratio curve is shown for reference. Both samples show some response to \( V_2 \), which is increased by annealing. By scaling the saturated \( V_2 \) response to overlap with the two sample responses a percentage of the positrons annihilating in \( V_2 \) in the Si at the SiOₓ/Si boundary can be obtained: 20 ± 2 and 47 ± 2% before and after annealing, respectively. This increase in vacancy response is either caused by an increase in the number of defects, possibly by the growth of the SiO₂ interface during annealing, or by an increase in the probability of trapping by vacancies already present. The oxygen responses deduced for both samples after removing the \( V_2 \) responses were found to be identical (≈3%), as expected from the overlap of the positron implantation profile with the oxide film. It is therefore unlikely that an increased sensitivity to \( V_2 \) would be due to a reduction of positron trapping in the oxides; the increase could, however, be caused by a change in the charge state of the vacancies (i.e., from positive to neutral or negative).

The \( S-W \) plots⁵ in Fig. 4 reveal the states in which positrons are annihilated and how the sensitivity to each state changes with varying \( E \); each specific annihilation site has an associated point on the \( S-W \) graph. The \( W \) parameter here is also normalized to unity for the bulk material. The large circles indicate the different states, as found with VEPFIT, within the samples. Both as-deposited and annealed samples have different surface and film states in which positrons are annihilated, where the different film response is thought to be due to varying oxygen content. Both also have some response to what is believed to be the defected Si. The annealed samples exhibit the most prominent response to vacancy-type defects, but the as-deposited samples also have a slight defect response, agreeing with the ratio curves and \( S(E) \) plots.

B. Different AlOₓ growth methods

To look at the differences between AlOₓ/SiO₂/Si samples grown by thermal ALD and sputtering on 0.8 Ω·cm FZ pSi, 30 nm-thick film samples were compared before and after annealing at 425 °C in N₂ for 30 min. The \( S(E) \) plot for the as-deposited sputtered film rises much more slowly toward unity with increasing \( E \) than for the ALD film, with a much reduced trapping response, as shown in Fig. 5. Once annealed, however, the response rapidly increases toward that of the thermal ALD samples, although it does not have the same defected Si interface feature. The \( S-W \) plot in Fig. 6 is used to determine the nature of the interface in the sputtered sample before and after annealing, in comparison with the ALD sample. The data for the sputtered sample shows
little or no response to the film or the defected Si state. The sputtered film/Si interface is highly trapping, particularly after annealing, but this appears not to be caused by defects in Si, but rather perhaps by an oxide response at the interface. The $S$-$W$ plot shows this interface state, as found with VEPFIT (thickness ~1 nm). The as-deposited sputtered film has an interface state that does not lie on the Si-$\text{AlO}_x$ $S$-$W$ line. This, along with the low $S$ and high $W$ parameters, indicates a high oxygen response, viz., a defected oxide state. Upon annealing the interface response now lies along the Si-$\text{AlO}_x$ line. This is still an oxide response, but the higher $S$ and lower $W$ parameters suggest an annealed oxide response, i.e., undefected oxide. The high negative fixed charge density seen in the thermal ALD samples appears to be either much weaker or not present in the sputtered samples, reducing the positron response to the film and increasing it in the SiO$_2$ layer. These differences may be the reason why ALD films are generally better passivating than those sputtered.$^{21}$

C. Thick films

The sputtering growth method was further investigated with thicker (740 nm) films to look better at the differences between the positron responses to the as-deposited and annealed films, and additionally the effects of the substrate type on $S(E)$. The $S$ parameter in the thick films appears to be on average lower than in all the thin films, indicating a greater response to oxygen, as seen in TiO$_2$ films.$^7$ As in the thin-film sputtered samples there is a difference in the positron response to the $\text{AlO}_x$ film after annealing, made more directly observable by the increased thickness, as shown in Fig. 7. The annealed films have a higher average $S$ parameter, which can also be seen on the $S$-$W$ plot in Fig. 8. This plot shows no evidence of any trapping interface state as seen in the thin ALD films (Figs. 4 and 6). It can also be seen in Fig. 8 that the films have a higher $W$ parameter before annealing, indicative of a higher oxygen content. This was verified in the ratio curves taken at $E = 5$ keV, shown in Fig. 9, where annealing causes a decrease in the size of the oxygen-related peak. Compared to the thin films the observed decrease in O response is much larger with a $21 \pm 2\%$ drop after annealing. The thick films start with a much greater O response than the thin films, caused either by more O atoms or by more vacancies. After annealing the thick film’s O response drops to a level similar to that in the

**FIG. 5.** (Color online) Normalized $S(E)$ plot for 30 nm AlO$_x$ films deposited by thermal ALD or by sputtering, before and after annealing at 425 °C in N$_2$ for 30 min.

**FIG. 6.** (Color online) Normalized $S$-$W$ plot for 30 nm AlO$_x$ film deposited by thermal ALD or by sputtering, before and after annealing at 425 °C in N$_2$ for 30 min. The large circles denote different states within the samples.

**FIG. 7.** (Color online) Normalized $S(E)$ plot for 740 nm AlO$_x$ film deposited by sputtering on p or n-type Si, before and after annealing at 425 °C in N$_2$ for 30 min.

**FIG. 8.** (Color online) Normalized $S$-$W$ plot for 740 nm AlO$_x$ film deposited by sputtering on p or n-type Si, before and after annealing at 425 °C in N$_2$ for 30 min. The large circles denote different states within the samples.
ALD creates an AlOₓ different in the samples grown by the two methods. Thermal growth method. The cause of this trapping, however, is samples have an interface which traps positrons, and annealing studied after annealing at 425°C with different substrate dopant types, and their evolution was characteristics. Here the films were grown by thermal ALD excellent probe of AlOₓ film and film and sputtering methods, to different film thicknesses and charge density in the AlOₓ within boundary. Thermal ALD is known to cause a high negative ping and annihilation occurring in the Si side of the SiOₓ lower effective positron diffusion length in the bulk Si. This last observation could be a result of band-bending at the SiOₓ/Si interface.\textsuperscript{22}

IV. CONCLUSION

This work has shown that positron techniques are an excellent probe of AlOₓ film and film/substrate interface characteristics. Here the films were grown by thermal ALD and sputtering methods, to different film thicknesses and with different substrate dopant types, and their evolution was studied after annealing at 425°C in N₂ for 30 min. All samples have an interface which traps positrons, and annealing has the effect of increasing this trapping response, regardless of growth method. The cause of this trapping, however, is different in the samples grown by the two methods. Thermal ALD creates an AlOₓ/SiOₓ/Si interface with positron trapping and annihilation occurring in the Si side of the SiOₓ/Si boundary. Thermal ALD is known to cause a high negative charge density in the AlOₓ within ~1 nm of the interface, inducing positive charge in the Si next to the interface. This positive charge reduces diffusion into the oxides and increases annihilation in the Si. In this region there is a V₂ response (20 ± 2%) before annealing which increases to 47 ± 2% after annealing. The data for both thin and thick sputtered films do not show any evidence for electrostatic shielding or positron trapping in defects in Si near the interface, but rather trapping occurs directly in the SiOₓ interface in the as-deposited sample, and the positron response to it increases after annealing, as an SiOₓ layer is formed. Annealing the film has the effect of lowering the film oxygen response in all film types.

ACKNOWLEDGMENTS

The authors are grateful to Dr. A. P. Knights (McMaster University) for instigating this collaborative research project. T-T.A.L., S.R., and A.C. acknowledge funding from the Australian Research Council.

\textsuperscript{12}K. G. Lynn and A. N. Goland, Solid State Commun. 18, 1549 (1976).
\textsuperscript{17}R. Krause-Rehberg and H. S. Leipner, Positron Annihilation in Semiconductors (Springer, Berlin, 1999).
\textsuperscript{19}K. G. Lynn and A. N. Goland, Solid State Commun. 18, 1549 (1976).
\textsuperscript{24}K. G. Lynn and A. N. Goland, Solid State Commun. 18, 1549 (1976).
\textsuperscript{34}J. A. Baker, P. G. Coleman, and N. B. Chilton, Vacuum 41, 1593 (1990).