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T. G. Allen and A. Cuevas

Citation: [Applied Physics Letters](#) **105**, 031601 (2014); doi: 10.1063/1.4890737

View online: <http://dx.doi.org/10.1063/1.4890737>

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Electronic passivation of silicon surfaces by thin films of atomic layer deposited gallium oxide

T. G. Allen^{a)} and A. Cuevas

Research School of Engineering, Australian National University, Canberra 0200, Australia

(Received 8 June 2014; accepted 1 July 2014; published online 21 July 2014)

This paper proposes the application of gallium oxide (Ga_2O_3) thin films to crystalline silicon solar cells. Effective passivation of n- and p-type crystalline silicon surfaces has been achieved by the application of very thin Ga_2O_3 films prepared by atomic layer deposition using trimethylgallium (TMGa) and ozone (O_3) as the reactants. Surface recombination velocities as low as 6.1 cm/s have been recorded with films less than 4.5 nm thick. A range of deposition parameters has been explored, with growth rates of approximately 0.2 Å/cycle providing optimum passivation. The thermal activation energy for passivation of the Si- Ga_2O_3 interface has been found to be approximately 0.5 eV. Depassivation of the interface was observed for prolonged annealing at increased temperatures. The activation energy for depassivation was measured to be 1.9 eV. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4890737>]

Recombination of charge carriers at the silicon surface, especially beneath the metallised contact regions, remains one of the biggest loss mechanisms in crystalline silicon (c-Si) solar cells.¹ An array of dielectric materials have been utilised for their capacity to suppress such defect-assisted Shockley-Read-Hall recombination, most notably silicon dioxide (SiO_2), silicon nitride, hydrogenated amorphous silicon (a-Si:H), and aluminium oxide (Al_2O_3). Other dielectrics, like hafnium oxide and amorphous silicon carbide, have also been shown to provide chemical and charge-induced passivation of recombination active surface states.

Gallium oxide (Ga_2O_3) is a wide bandgap ($E_g \approx 4.23$ –5.24 eV), optically transparent semiconductor.² Though typically non-conductive in its stoichiometric form, Ga_2O_3 can be doped with either silicon or tin for n-type conductivity.³ Gallium, like aluminium, is also a p-type dopant in silicon, and so Ga_2O_3 has the potential to be used as a p-type dopant source via thermal diffusion or laser processing. Additionally, the energy band structure of Ga_2O_3 suggests that it could be utilised as a carrier-selective contact to crystalline silicon.⁴

These properties have prompted research into the application of Ga_2O_3 to photovoltaics. Chandiran *et al.*⁵ have applied Ga_2O_3 to a dye-sensitized solar cell as an electron tunnelling interlayer between the porous, electron-collecting TiO_2 layer, and the absorbing dye. The application of Ga_2O_3 reduced the electron back reaction into the electrolyte, resulting in an increase in the open circuit voltage (V_{oc}) of the device. Recently, both Minami *et al.*⁶ and Lee *et al.*⁷ used Ga_2O_3 as a buffer layer between the p-type Cu_2O and electron collecting ZnO:Al in cupric-based heterojunction thin film solar cells. The application of the Ga_2O_3 buffer layer to the cupric-AZO interface reduced the recombination of charge carriers while permitting electron transfer to the negative terminal of the device, thereby enhancing V_{oc} .

Despite these demonstrated qualities, and gallium oxide's known ability to passivate GaAs⁸ and reduce the density of surface defects in strained silicon,⁹ no attempt has yet been made to study this material on c-Si for photovoltaic applications. In this Letter, we provide evidence of surface passivation of crystalline silicon by Ga_2O_3 prepared by atomic layer deposition (ALD).

Ga_2O_3 thin films were prepared by ALD on 4–5 Ω cm n-type and 2–3 Ω cm p-type FZ <100> silicon in a Beneq TFS 200 ALD reactor with trimethylgallium (TMGa) and ozone (O_3) used as the reactants. A 200 μm diameter orifice was installed between the precursor and reactor to limit the precursor dose. All of the silicon samples were saw-damage etched in TMAH, cleaned in the standard RCA process, and immersed in a dilute HF solution prior to deposition. Variable angle spectroscopic ellipsometry (J.A. Woolam M2000D) was performed on polished samples that were also immersed in HF prior to Ga_2O_3 deposition in order to measure the thickness of the deposited films. A Tauc-Lorentz model was used to fit the ellipsometry data.

The effective minority carrier lifetime (τ_{eff}) was measured as a function of the excess carrier concentration (Δn) on symmetrically deposited lifetime structures using a Sinton Instruments WCT-120 photoconductance tool operating in the photoconductance decay (PCD) transient mode for the annealed samples, and in the quasi-steady-state (QSS) generalized mode for the as-deposited samples. All lifetime samples have been annealed in a forming gas ambient composed of 5% H_2 /95% Ar after initial comparisons with N_2 annealing resulted in a considerable improvement in τ_{eff} .

Figure 1 plots the as-deposited Ga_2O_3 film thickness and post-anneal (400 °C for 15 min in forming gas) τ_{eff} against deposition temperature. All depositions comprised 200 ALD cycles. The range in deposition rate (0.13–0.62 Å/cycle) is slightly greater than that reported by Comstock and Elam (0.2–0.5 Å/cycle) over the same temperature range.¹⁰ From Figure 1, an observable optimum deposition temperature window for surface passivation exists between 200 and 250 °C with the maximum in minority carrier lifetime

^{a)} Author to whom correspondence should be addressed. Electronic mail: thomas.allen@anu.edu.au

FIG. 1. As-deposited Ga_2O_3 film thickness and post-anneal minority carrier lifetime (τ_{eff}) on 4–5 Ω cm n-type silicon plotted as a function of deposition temperature. All depositions comprised 200 ALD cycles. The lines serve as guides for the eyes.

corresponding to Ga_2O_3 films as thin as 2.85 nm. The deposition rate in this window ranges from 0.14 to 0.22 $\text{\AA}/\text{cycle}$, approximately a quarter of the deposition rate at 400 °C (0.63 $\text{\AA}/\text{cycle}$) and much lower than ALD Al_2O_3 using TMA at similar temperatures (approximately 1–1.5 $\text{\AA}/\text{cycle}$). Donmez *et al.* have reported a steadier growth rate using TMGa and O_2 plasma with a temperature-independent growth rate of 0.53 $\text{\AA}/\text{cycle}$ reported in the deposition window of 100–400 °C.¹¹ Dezzlah *et al.* also report on atomic layer deposited Ga_2O_3 with $\text{Ga}_2(\text{NMe}_2)_6$ and H_2O with growth rates in excess of 1 $\text{\AA}/\text{cycle}$ for deposition temperatures between 150 and 250 °C: similar to TMA- H_2O Al_2O_3 thermal ALD deposition rates.¹²

A deposition temperature of 250 °C was used for further study of the annealing parameters because of its favourable initial passivation results and growth rate. Float zone, 4–5 Ω cm n-type samples deposited at 250 °C were annealed in forming gas at a range of temperatures between 300 and 450 °C in order to derive the optimum anneal conditions. The results are plotted in Figure 2.

The x-axis in Figure 2 denotes the cumulative anneal time t_{an} for a double-side deposited sample; the y-axis represents the τ_{eff} measured at an injection level of $\Delta n = 1 \times 10^{15} \text{ cm}^{-3}$. The optimum annealing condition—180 min at 350 °C—resulted in a minority carrier lifetime of approximately 2.5 ms and an upper limit to the surface recombination velocity (SRV) of 6.1 cm/s, where the Auger parameterization of Richter *et al.*¹³ was used to calculate the bulk lifetime. This compares to a τ_{eff} of 9.5 ms and an SRV of 1.5 cm/s for a similar sample passivated with 20 nm of plasma-assisted ALD Al_2O_3 and annealed in forming gas for 30 min at 425 °C. Spatially resolved τ_{eff} maps for both n- and p-type Ga_2O_3 passivated samples are displayed in Figure 3.

From Figure 2, it is evident that the rate of activation of the passivation is increasing with temperature. The optimum annealing time (t_{an}) for each annealing temperature (T_{an}) also results in an increase in the maximum observed τ_{eff} as T_{an} decreases, with the exception of $T_{\text{an}} = 300$ °C where a

FIG. 2. Minority carrier lifetime as a function of cumulative annealing time. The dashed curves represent the modelled data using Eq. (1). The as-deposited data are shown at $t_{\text{an}} = 0$.

maximum in τ_{eff} had not been reached after over 9 hours of annealing. A similar effect is observable for the reverse, depassivation reaction for temperatures greater than 300 °C: as the annealing temperature increases, the rate at which the interface depassivates also increases. After the initial activation of the passivation, the lifetime decreases to an equilibrium value (approximately 100 μs), greater than the as-deposited lifetime (approximately 10 μs), indicating that some passivation of the interface is retained.

An exponential model has been applied to fit the $\tau_{\text{eff}}(t_{\text{an}}, T_{\text{an}})$ data to further analyse the passivation and depassivation reactions. The model is based on that of Mitchell *et al.*, who applied an exponential fit to temperature and time dependent τ_{eff} data from a-Si:H-passivated silicon surfaces,¹⁴ and Dingemans *et al.*, who applied the same model to SiO_2 - Al_2O_3 stacks on c-Si.¹⁵ The exponential model has been extended to account for both the passivation and depassivation of the Si- Ga_2O_3 interface

$$\frac{1}{\tau_{\text{eff}}} = [a + b \exp(-t_{\text{an}}/R_{\text{pass}})] + [c - d \exp(-t_{\text{an}}/R_{\text{depass}})], \quad (1)$$

where the first bracketed term represents the exponential fitting to the passivation data, and the second bracketed term represents the exponential decay associated with the depassivation data. The parameters R_{pass} and R_{depass} are the time constants of the passivation and depassivation reactions. These reaction time constants are then used to extract the activation energies for both the passivation and depassivation reactions according to the Arrhenius equation

$$R_{(de)pass} = A \exp\left(-\frac{E_A}{k_B T_{\text{an}}}\right). \quad (2)$$

The dashed curves in Figure 2 represent the summed exponential model of Eq. (1) applied to the measured values of τ_{eff} . The divergence of the model from the data in Figure 2 can be ascribed to a number of factors. The use of a single

FIG. 3. Spatially resolved minority carrier lifetime maps from PL images of (a) Ga_2O_3 -passivated 4–5 Ω cm n-type and (b) 2–3 Ω cm p-type silicon, both annealed at 375 $^\circ\text{C}$ for 50 min in forming gas. The images reveal a uniform passivation across the wafer surface. Note the difference in scale between the two images.

sample for each T_{an} study introduces some uncertainty in τ_{eff} , resulting in an artificial stretching of the curves along the x -axis and compression in the y -axis. Also, if the mechanism for passivation involves the interaction with another chemical species (hydrogen, for example, is commonly identified as a passivating mechanism for surface defects in crystalline silicon^{14–17}), then the availability of that species is not accounted for in the model. The results, for example, are consistent with the progressive effusion of hydrogen from the Si- Ga_2O_3 interface with increasing annealing temperature and time after the observed peak in τ_{eff} . This hypothesis of a reaction mechanism that involves a limited and diminishing source of one species may also account for the better fitting of the model to the data for annealing times after the peak in passivation is achieved. Despite these possible limitations, the model does provide a reasonable fit to the lifetime data.

The Arrhenius plots of Figure 4 display the extracted reaction time constants of Eq. (1) as a function of inverse energy. The plotted symbols in Figure 4 give the best fits to both the τ_{eff} data and the Arrhenius model of Eq. (2). The error bars in the plot represent the upper and lower bounds in reaction rate values that still give a credible fit to the data in

FIG. 4. Arrhenius plot of the reaction rate ($R_{(de)pass}$) extracted from Eq. (1). The error bars in R represent the upper and lower bounds in reaction rate values that give a credible fit to the data in Figure 2. The error bars in the extracted activation energies are the values of E_A extracted from the bounds in possible R values.

Figure 2, and so they are not directly representative of the error in the reaction rate, which is difficult to quantify given the reasons outlined in the discussion above.

The application of Eq. (2) to the reaction rates of Eq. (1) indicates an activation energy E_A of approximately 0.5 eV for the passivation reaction and 1.9 eV for the depassivation reaction. The error bars in the inset graph of E_A in Figure 4 correspond to the activation energies extracted from the error bar values for the reaction rates. Therefore, they are not indicative of the error in the fits of Eq. (2) to the plotted data in the figure, which is small, but rather represent a range of possible, albeit less likely, values for E_A .

The approximate activation energy for passivation extracted from the data in Figure 4 (0.5 eV) is similar to the values reported by Mitchell *et al.*¹⁴ (0.67 eV) and de Wolf and Kondo¹⁶ (0.6 eV) for the activation of a-Si:H; and outside the range reported by Richter *et al.*¹⁷ (1.4–1.5 eV) and Saint-Cast¹⁸ (1.5 eV) for Al_2O_3 films, and Dingemans *et al.*¹⁵ (0.9 and 1.2 eV) for Al_2O_3 - SiO_2 stacks. Mitchell *et al.* suggest that the lower activation energies for a-Si:H indicate an interfacial hydrogen dependency on passivation, rather than a bulk hydrogen effusion process.¹⁴ Conversely, Richter *et al.* claim that the higher activation energy for Al_2O_3 passivation relates to both the existence of an interfacial SiO_2 layer, citing the similar activation energy of Stesmans¹⁹ for the Si- SiO_2 interface, and the diffusion of hydrogen from the bulk of the Al_2O_3 film. The diffusion of bulk hydrogen from Al_2O_3 films to passivate the Si- SiO_2 interface is further demonstrated in Ref. 15. Richter *et al.* further attribute the passivation of the interface to structural changes in the Al_2O_3 film which could be a factor in the annealing behaviour of the Ga_2O_3 films.¹⁷

For the Ga_2O_3 passivation studied in this work, uncertainty in E_A and the as-yet unknown properties of the material itself, compared to the other films studied using this technique, does not support such strong conclusions regarding the nature of the passivation mechanism. What can be concluded from the data is that the difference in the passivation and depassivation activation energies is not as great as for a-Si:H, Al_2O_3 or SiO_2 passivation dielectrics. This could have implications relating to the stability of the passivation, and for the potential thermal processing windows if Ga_2O_3 were to be incorporated into a photovoltaic device.

Very thin films of ALD deposited gallium oxide (Ga_2O_3) have been shown to effectively passivate n- and p-type silicon surfaces, with an optimum post-deposition

annealing condition (350 °C for 180 min) resulting in a minority carrier lifetime of 2.5 ms on 4–5 Ω cm n-type silicon. Photoluminescence (PL) imaging of the passivated wafers show a uniformity in passivation across the 4 in. wafer surface. The annealing temperature and time dependence of τ_{eff} have been modelled using a sum of two exponentials in order to calculate the activation energies for the passivation and depassivation reactions: approximately 0.5 and 1.9 eV, respectively.

The authors would like to thank Dr. D. Macdonald for his many suggestions and help in preparing the manuscript. This work has been supported by the Australian government through the Australian Renewable Energy Agency (ARENA). Ellipsometer facilities at the Australian National Fabrication Facility were used in this work.

¹R. M. Swanson, in *Proceedings of the 31st IEEE Photovoltaic Specialists Conference*, 2005.

²F. K. Shan, G. X. Liu, W. J. Lee, G. H. Lee, I. S. Kim, and B. C. Shin, *J. Appl. Phys.* **98**, 023504 (2005).

³S. Ohira, N. Suzuki, N. Arai, M. Tanaka, T. Sugawara, K. Nakajima, and T. Shishido, *Thin Solid Films* **516**, 5763 (2008).

⁴J. Robertson, *Thin Solid Films* **516**, 1419 (2008).

⁵A. K. Chandiran, N. Tetreault, R. Humphry-Baker, F. Kessler, E. Baranoff, C. Yi, M. K. Nazeeruddin, and M. Grätzel, *Nano Lett.* **12**, 3941 (2012).

⁶T. Minami, T. Miyata, and Y. Nishi, *Sol. Energy* **105**, 206 (2014).

⁷Y. S. Lee, D. Chua, R. E. Brandt, S. C. Siah, J. V. Li, J. P. Mailoa, S. W. Lee, R. G. Gordon, and T. Buonassisi, *Adv. Mater.* **26**(27), 4704–4710 (2014).

⁸M. Passlack, M. Hong, E. F. Schubert, J. R. Kwo, J. P. Mannaerts, S. N. G. Chu, N. Moriya, and F. A. Thiel, *Appl. Phys. Lett.* **66**, 625 (1995).

⁹S. Pal, S. K. Ray, B. R. Chakraborty, S. K. Lahiri, and D. N. Bose, *J. Appl. Phys.* **90**, 4103 (2001).

¹⁰D. J. Comstock and J. W. Elam, *Chem. Mater.* **24**, 4011 (2012).

¹¹I. Donmez, C. Ozgit-Akgun, and N. Biyikli, *J. Vac. Sci. Technol., A* **31**, 01A110 (2013).

¹²C. L. Dezhlah IV, J. Niinisto, K. Arstila, L. Niinisto, and C. H. Winter, *Chem. Mater.* **18**, 471 (2006).

¹³A. Richter, S. W. Glunz, F. Werner, J. Schmidt, and A. Cuevas, *Phys. Rev. B* **86**, 165202 (2012).

¹⁴J. Mitchell, D. Macdonald, and A. Cuevas, *Appl. Phys. Lett.* **94**, 162102 (2009).

¹⁵G. Dingemans, F. Einsele, W. Beyer, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **111**, 093713 (2012).

¹⁶S. de Wolf and M. Kondo, *Appl. Phys. Lett.* **90**, 042111 (2007).

¹⁷A. Richter, J. Benick, M. Hermle, and S. W. Glunz, *Appl. Phys. Lett.* **104**, 061606 (2014).

¹⁸P. Saint-Cast, Ph.D. dissertation, University of Konstanz, 2012.

¹⁹A. Stesmans, *Appl. Phys. Lett.* **68**, 2076 (1996).