Metal oxide sol-gel films for protection of ultrathin polysilicon contacts

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Introduction

Polysilicon (poly-Si) passivating contacts have been successfully integrated with crystalline silicon solar cells, demonstrating efficiencies greater than 26% [1]. There has also been a notable shift of interest towards poly-Si contacts in industrial mass production [1][2]. One pathway to further advance this technology is to thin the polysilicon layer (i.e. < 20 nm), reducing its parasitic absorption and material usage. However, the passivation degradation of thin poly-Si layers due to metallisation can be significant, especially when subjecting the poly-Si/metal stack to a thermal anneal. As such, there is interest in devising a solution to protect the poly-Si contacts, whereby its passivation is retained at elevated temperature without significantly compromising contact resistivity. This abstract focuses on the development of simple solution-based protective layers between the poly-Si and metal electrode to minimise passivation degradation. The solution-based approach also offers the advantages of single-side deposition at room temperature. In this study, we demonstrate that nanoparticle solution-based interlayers, aluminium doped zinc oxide (AZO) and tin oxide ($\mathrm{SnO_2}$), improve the thermal stability of thin poly-Si/metal contacts up to 500 °C.

Experiment

In this study, we investigated three nanoparticle solutions as protective coatings for 10 nm n^+poly-Si/SiO_2 contacts, evaluating their impact on both contact resistivity and passivation. Firstly, n-type silicon wafers (~2 Ω-cm) are deposited with a symmetrical structure of 1.2-1.6 nm of SiO_2 and 10 nm n^+poly-Si. These stacks are then annealed at high temperature to activate the dopants, resulting in implied open circuit voltages iV_{oc} of ~710mV measured via QSSPC (quasi-steady state photoconductance) measurements.

To make contact resistivity ρ_c samples, the above substrates were first immersed in a dilute HF etch to remove the native oxide layer on top of poly-Si films. Following this, thin metal oxide films were spin-coated from nanoparticle sol-gel solutions at different spin speeds, followed by a post-bake at 120 °C to eliminate the solvents, resulting in different thicknesses as summarised in Table 1. The two AZO films trialled, labelled as high WF AZO and low WF AZO, differ in the work function that they provide. The manufacturer lists the work function of these two films as -4.3eV and -3.9 eV, respectively. The thicknesses of these films were measured by spectroscopic ellipsometry. Finally, a 200 nm Al layer was deposited by thermal evaporation through a shadow mask to make a Cox and Strack pattern [3]. These samples also had a full-area Al layer on the rear-side. Contact resistivity values were extracted using the “model-E” approach in reference [3].

Table 1. Details of nanoparticle solutions and their thickness via different spin coating speeds. LWF = low work function. HWF = high work function.

Film Composition	Spin Speed (rpm)	Thickness (nm)	Manufacturer/Product Name/ No.
$\mathrm{SnO_2}$	2000	27.2	Avantama / N-30-Flex / 9075

SnO_2	6000	49.2	Avantama / N-30-Flex / 9075
$Al:ZnO$ LWF	2000	39.0	Avantama / N-21X-Flex, 10023
$Al:ZnO$ LWF	6000	20.8	Avantama / N-21X-Flex / 10023
$Al:ZnO$ HWF	2000	39.0	Avantama / N-20X-Flex / 10022
$Al:ZnO$ HWF	6000	20.8	Avantama / N-20X-Flex / 10022

For examination of passivation quality, sister samples were prepared on the same n^+poly-Si/SiO_2/c-Si/SiO_2/n^+poly-Si substrates, with full-area spin coated SnO_2 and AZO films. These were then patterned with half-area Al (~200 nm) leaving the other half non-metallised. The PL image provided insight into regions with higher lifetime, as distinguished by higher PL counts. Reference samples with no metal oxide thin films (i.e. directly metallised samples) were fabricated as a comparison for both passivation and ρ_c samples.

Key Results

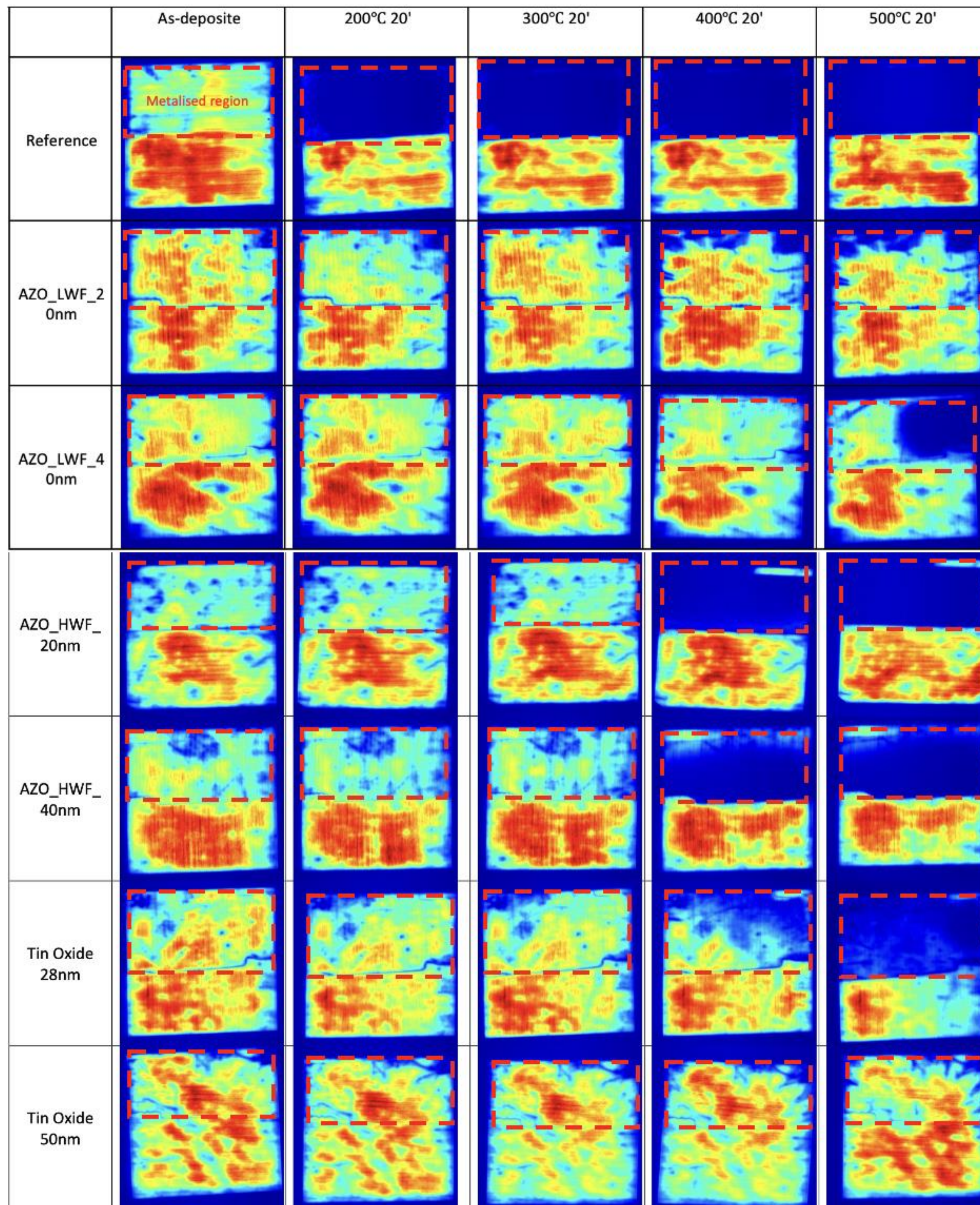

Figure 1. PL images of n^+poly-Si/metal oxide/Al contacts as a function of accumulative anneal steps. The red dashed box shows the region of Al metalisation.

Figure 1 presents the PL images of passivation samples as a function of cumulative annealing steps. Regions with Al metallization are marked by the dashed red squares. The first row of the figure shows the PL image of a sample without a protective interlayer. Notably, the passivation quality from the metallized region is markedly diminished compared to the non-metallized region, even at low temperatures ~200°C. The subsequent rows illustrate the stability enhancement afforded by the protective metal oxide layers. It can be seen that both low WF AZO and SnO_2 provide decent protection up to 400-500°C, as their metallised regions have similar PL counts to the non-metallised regions. The passivation degradation seen for the other samples at and beyond 400ºC may be

attributed to penetration of Al through the interlayer and poly-Si/SiO_2 layers to the c-Si interface which introduces recombination centres.

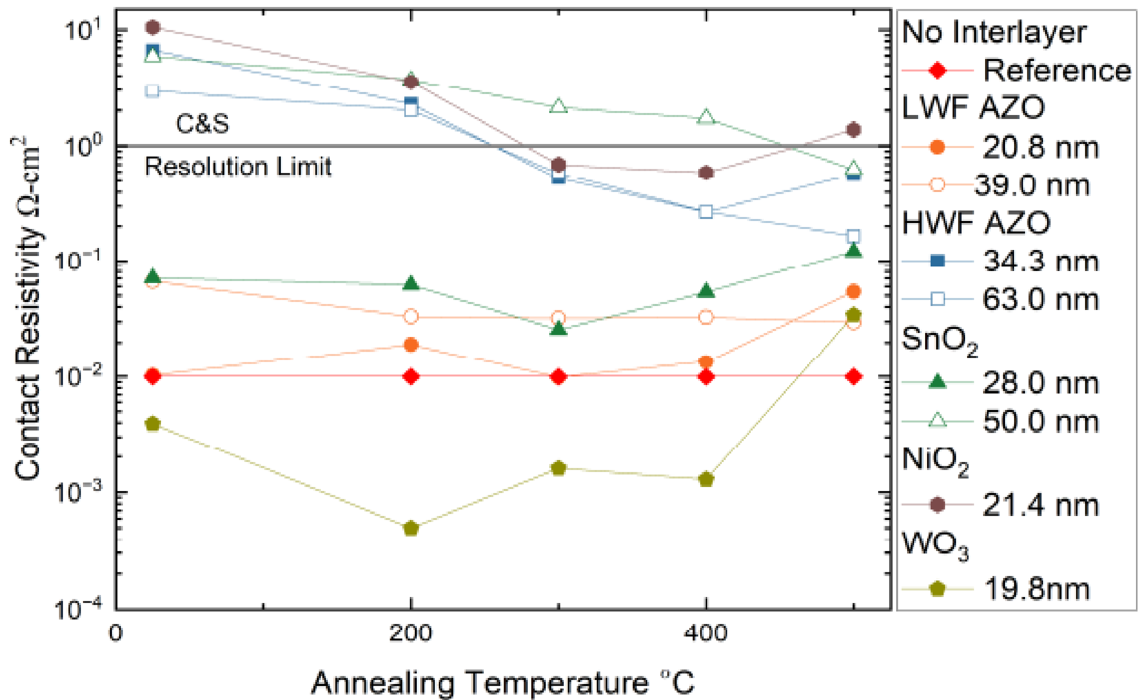

Figure 2. Contact resistivity values of n⁺poly-Si/SiO_2 contacts with and without metal oxide interlayers vs. successive annealing steps. The grey line shows the estimated upper resolution limit for the Cox and Strack method (values higher than this point are likely to be inaccurate).

While protection of the n^+poly-Si/SiO_2 stack surface passivation is the primary aim of this study, this must be done whilst still allowing usable ρ_c values. Figure 2 presents the ρ_c values of samples with three different metal oxide interlayers, each with two thicknesses, as a function of cumulative annealing steps from 200-500 °C. The ρ_c of the samples without any interlayer is represented by the red line and has a consistently low ρ_c value of ~ 0.01 Ωcm^2 throughout the annealing process. As expected, all samples with interlayers have higher ρ_c values. Among these the high WF AZO films have the lowest ρ_c values, with both thin and thick films maintaining values below 0.1 Ωcm^2 across the temperature range. However, as discussed above these interlayers were found to provide only minimal passivation protection. The low WF AZO films, which were found to provide better passivation protection, have significantly higher ρ_c values which reduce after annealing to values around 0.17 Ωcm^2. It is interesting to note that both of the AZO films show very little ρ_c dependence on the thickness of the films, indicating that the resistivity is dominated by interfacial, rather than bulk, resistances. Conversely, the SnO_2 interlayers are found to exhibit a strong dependence on the layer thickness in the as-deposited state. However, after annealing the ρ_c difference between these samples decreases settling at 0.16 Ωcm^2 and 0.06 Ωcm^2 at 400°C for thick and thin films, respectively. Hence, considering both the PL and ρ_c behaviour of the metal oxide films it can be concluded that the low WF AZO and SnO_2 films provide excellent protection up to 500°C whilst maintaining ρ_c values sufficiently low for full-area contacts in high efficiency silicon solar cells.

Conclusion

This study explores the enhancement of thermal stability for thin n^+poly-Si/SiO_2 passivating contacts by inserting solution deposited metal-oxide based films between the Al and poly-Si layers. The PL

images indicate that protection up to 500°C can be achieved using a 50 nm SnO_2 layer, or a 20-40 nm low WF AZO layer. In terms of contact resistivity, SnO_2 samples maintained a moderate ρ_c of 0.62 Ω-cm^2 and the low WF AZO layers maintained ρ_c values of 0.6-0.1 Ω-cm^2 at 500°C. These promising initial results indicate the possibility of using solution deposited SnO_2 and AZO thin films as interlayers between n^+poly-Si/SiO_2 contacts and their Al electrodes, to protect the surface passivation at temperatures up to 500°C.

References

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