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Atomic layer deposited dielectric and/or semiconducting oxide bilayers for crystalline silicon surface passivation

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Abstract

This study deals with the silicon surface passivation by thermal ALD deposited oxides bilayer of $\text{HfO}_2/\text{Al}_2\text{O}_3$ as well as single layer of Al rich ZnO (AZO) in the form of ZnO and Al_2O_3 multilayers. A significant improvement in the effective minority carrier lifetime ($\tau_{\text{eff}} \sim 1.3\text{ms}$) of n-type Si is observed after deposition of $\text{HfO}_2(5\text{nm})/\text{Al}_2\text{O}_3(5\text{nm})/\text{Si}$ compared to that of the single layer $\text{Al}_2\text{O}_3(10\text{nm})/\text{Si}$ ($\sim 0.6\text{ms}$). Better surface passivation is due to a significant increase in the effective charge density in the bilayer system. Also, the sequence of the dielectric layers is found to play an important role in the quality and effectiveness of the passivation. Further, high τ_{eff} ($\sim 1.5\text{ms}$) is also realized for p-type Si passivated by ALD deposited AZO films as compared to single layer of pure ZnO ($\sim 35\mu\text{s}$) when annealed in hydrogen ambient at 450°C for 30mins.

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Keywords: Crystalline silicon; surface passivation; atomic layer deposition; dielectric and semiconducting oxides.

1. Introduction

Few nano-meters thick dielectric and semiconducting layers such as Al_2O_3 , Si_3N_4 , SiO_2 and a-Si:H are the key components in today's high efficiency silicon solar cells due to their excellent material properties for surface passivation which may also provide light management if the desired thickness of dielectric layers are made [1,2]. These layers ensure high level of chemical passivation by effectively reducing the density of silicon surface states. Additionally, the dielectric materials provide strong field-effect passivation due to the existence of high density of intrinsic fixed charges. However, futuristic higher efficiency solar cell concepts demand additional functionalities such as high degree of passivation and electrical conductivity of the nanomaterials [3]. It is also possible to

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manipulate built-in charges in the dielectrics by a combination of dielectric nano-layers. These functionalities can be realized in multi-oxide nano-laminates including SiO₂, Al₂O₃, HfO₂ and ZnO sublayers. This area is not well explored despite large number of reports using single layer system.

We report the increase of right kind of built-in charges by a suitable combination of high-k dielectrics which enhances the field-effect passivation of the n-type Si surface. Also, we show the excellent chemical passivation of p-type Si surface by a semiconducting oxide film of AZO made by alternate layers of ZnO and Al₂O₃.

2. Field-effect passivation of n-type silicon surface by stack of ALD deposited Al₂O₃ and HfO₂ bilayers

Single layer of Al₂O₃ (10nm thick) or bilayers of HfO₂/Al₂O₃ (5nm each) or Al₂O₃/HfO₂ (5nm each) are deposited on both sides of n-type Si (FZ, 2.5Ω, 325μm) at 300°C by thermal ALD process to make symmetrically passivated surfaces. Tri-methyl aluminium (TMA) and tetra-kis ethyl methyl amino hafnium (TEMAHf) are the precursors used for Al₂O₃ and HfO₂ layers with water as an oxidant. Post-deposition annealing of all the samples is done at temperature (T_{ani}) of 400°C in N₂ ambient for 105s and 600s in an RTP system. This is essential for the activation of passivation. MIS structures are made with electron beam evaporated Al of 1mm diameter through a metal mask for gate contact as well as full area Al coverage for back Si contact.

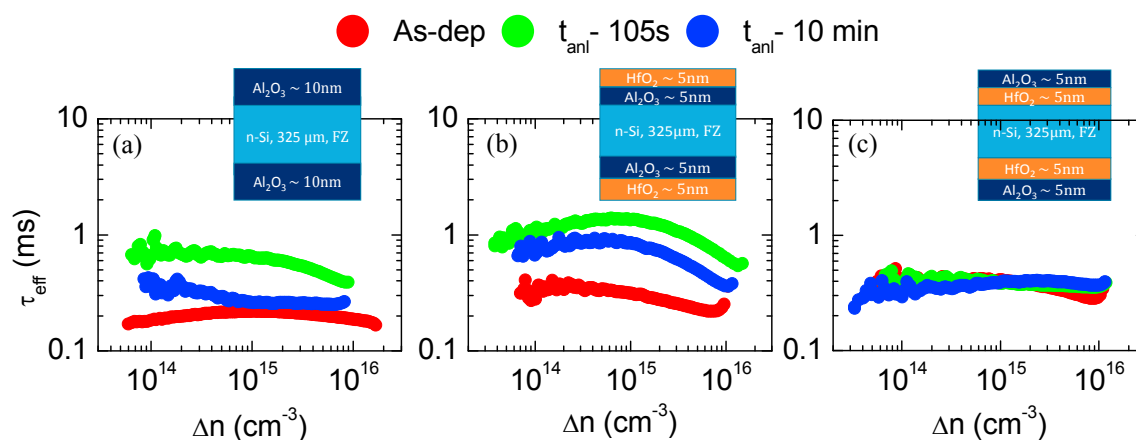


Fig. 1. Injection level dependent minority carrier lifetime of n-type Si symmetrically passivated with a) 10 nm Al₂O₃, b) 5nm HfO₂/5nm Al₂O₃ and c) 5nm Al₂O₃/5nm HfO₂. The best results are obtained in HfO₂/Al₂O₃ bilayer system.

Fig. 1 shows the injection level dependent minority carrier lifetime of n-type Si symmetrically passivated by oxide systems consisting of single layer Al₂O₃ or bilayer of HfO₂ and Al₂O₃ on silicon. It is clear that effective minority carrier lifetime (τ_{eff}) is improved with 5nm HfO₂/5nm Al₂O₃/Si (case b) compared to the single layer of 10nm Al₂O₃ (case a). On the other hand, the bilayer oxide system Al₂O₃/HfO₂/Si (case c) does not exhibit any improvement in the lifetime values after annealing.

The upper limit of surface recombination velocity (SRV) at the injection level (Δn) equal to 10¹⁵ cm⁻³ is calculated from the measured injection level dependent τ_{eff} using Sinton's lifetime tester (Model: WCT-120) assuming very large (infinite) bulk lifetime value and the results are shown in the figure 2a. The lowest value of SRV is 12cm/s which corresponds to the HfO₂/Al₂O₃/Si structure annealed for 105s. The single layer of Al₂O₃ shows a decrease in SRV values from 86 cm/s (as-deposited) to 25.3 cm/s after 105s annealing in N₂, which however, increases to ~ 62cm/s after 10 min annealing in the same ambient. It is important to note that the bilayer system Al₂O₃/HfO₂/Si does not exhibit any improvement in passivation performance after annealing under the same conditions. This indicates that the layer sequence is rather critical to realize surface passivation. The C-V measurement (Fig. 2b) reveals that the bilayer structure HfO₂/ Al₂O₃/Si exhibit enhanced effective oxide charge density (Q_{eff}) and a large hysteresis is seen as compared to the single layer Al₂O₃ or the bilayer Al₂O₃/HfO₂/Si. The

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