LNQE Laboratorium für Nano- und Quantenengineering

Leibniz Universität Hannover

Al_2O_3-passivation layers for Si-based solar cells

Florian Werner[1], Christoph Tegenkamp[2,*], Rolf Brendel[1,*] and Jan Schmidt[1]

[1] *Institute for Solar Energy Research Hameln (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany*
[2] *Institute for Solid State Physics, Leibniz University Hannover, Appelstr. 2, 30167 Hannover, Germany*
[*] *Laboratory for Nano- und Quantum Engineering (LNQE), Schneiderberg 39, 30167 Hannover, Germany*

Motivation:

One of the key parameter for solar cells is the surface recombination velocity of the charge carriers which limits the efficiency of photovoltaic devices. Therefore, a homogenous surface passivation with excellent electronic properties is demanding for future applications. There are two complementary contributions for a reduction in the surface recombination velocity: a reduction in the density of electronic surface states ('chemical passivation') and, secondly, a reduction in the electron or hole concentration near the surface, e.g., by a band bending in Si-surface toward the interface ('field-effect passivation'). Al_2O_3 films grown by atomic layer deposition (ALD) on crystalline silicon (c-Si) were shown to exhibit both contributions due to a well-defined interface structure and a high negative fixed charge density localized with in 1nm of the interface. In this joint project the chemical and electrical properties of passivation films have been studied by means of X-ray photoelectron spectroscopy (XPS) and capacitance-voltage (CV) analysis, respectively. Details of this project have been published recently (see J. Appl. Phys., 109, 113701 (2011).)

Results & Discussion:

Oxide films have been deposited via ALD which allows to grow high quality films in a layer-by-layer fashion by cycles of two half-reactions: in a first step the trimethyl aluminum (TMA) molecules react with the hydroxyl groups attached to the silicon surface , while in a second step the molecules are oxidized either by H_2O (so-called thermal ALD) or oxygen radicals created in an O_2-plasma (plasma-ALD).

Figure 1 shows effective lifetimes τ_{eff} measured at an injection density of $\Delta n=10^{15}$ cm^{-3} on 1.5 Ωcm p-type FZ-Si wafers passivated by Al2O3 films deposited by plasma-assisted and thermal ALD, respectively. As obvious, the lifetimes depend on thickness of the films as well as the film thickness. An excellent surface passivation quality is observed for ultrathin Al_2O_3 layers with a thickness <5 nm for plasma-assisted ALD and <10nm for thermal ALD.

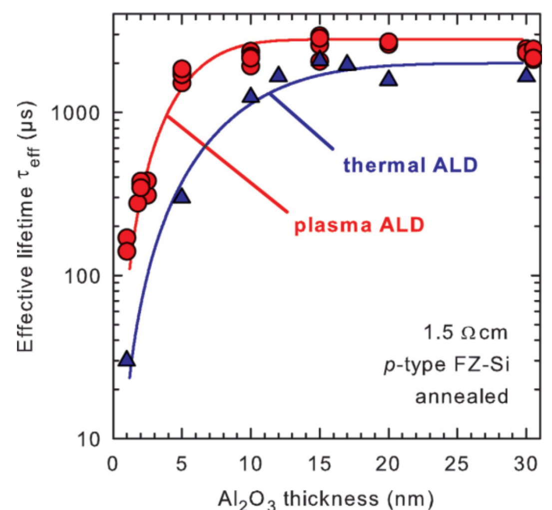

Figure 1: Effective lifetime τ eff at an injection density $\Delta n=10^{15}$ cm^{-3} measured on 1.5 Ωcm p-type FZ-Si passivated by Al_2O_3 films of varying thickness, deposited by plasma-assisted and thermal ALD.

In order to elucidate the origin of the thickness dependency we have performed XPS measurements which allow controlling the stoichiometry and analyzing the chemical composition at the interface (Fig.2). For samples coated with only one ALD cycle, no aluminum is detected at all, indicating that at least one "starting cycle" is required to generate a suitable nucleation surface for the ALD process. In addition, a negligible oxygen concentration is detected for the samples which received an HF dip prior to deposition. After five ALD cycles, an aluminum-to-oxygen ratio of 1:10 is calculated from the integrated intensities of the Al-2p and O-1s peaks. Subtracting the oxygen contribution of the interfacial SiOx layer yields an Al:O ratio of 1:8, which is far from the stoichiometric 1:1.5 atomic ratio. The Al:O ratio increases for thicker layers, yielding ratios of 1:3.7 for 30 cycles and 1:2.8 for 125 cycles, respectively, as shown in Fig.2. From this we conclude that in the native state or after an HF dip, the functional surface groups on the silicon wafer are not optimal for an adsorption of the TMA precursor molecules, which leads to an incomplete reaction of the TMA and, consequently, an increased relative oxygen concentration at the interface.

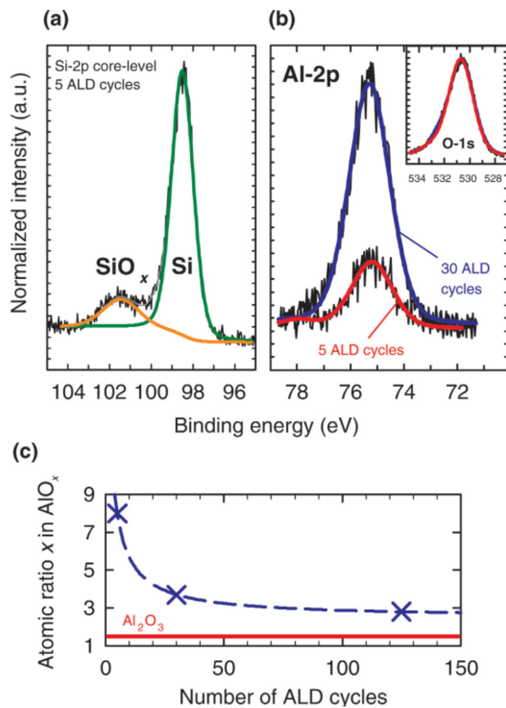

Figure 2: (a) Si-2p core-level peak recorded by XPS (hn=1253 eV) on a sample exposed to five ALD process cycles. The distinct double-peak structure corroborates a partial oxidation of the Si/Al_2O_3 interface. (b) Al-2p and O-1s core-level peaks for samples exposed to five and 30 ALD process cycles, respectively. The intensity was normalized to yield the same O-1s peak intensity. (c) Atomic ratio x in the AlO_x calculated from the relative intensities of the Al-2p and O-1s core-level peaks as a function of ALD cycles. The red line marks the expected stoichiometric ratio of x=1.5.

As we will show below the Al_2O_3 film exhibits further a fixed negative charge giving rise to field-effect passivation. Since no clear XPS double-peak structures are resolved for the aluminum and oxygen peaks besides the contribution from the interfacial SiO_x, both species are assumed to be present in only one charge state. Consequently, a single atomic species cannot sufficiently well explain the origin of the high negative fixed charge density. We propose the high oxygen-to-aluminum ratio caused by the incomplete ALD process during the first cycles as a candidate for the origin of the high negative charge density at the interface. Nonetheless, already after five ALD cycles neither the thickness of the SiO_x interface nor the Al:O ratio for a given thickness depends on the post-deposition anneal or the chemical pre-treatment of the sample.

The electronic properties of the interface have been quantified further by CV- spectroscopy and Corona-charge analysis. These methods are powerful tools in order to calculate the interface state density (D_{it}) and fixed charge density (Q_f). Figure 3 shows both quantities for a wide range of Al_2O_3 film thickness values, where the Al_2O_3 layers were deposited by plasma-assisted ALD. The ultralow surface recombination velocities routinely obtained on p- and n-type silicon are predominantly attributed to a strong field effect passivation caused by a high negative fixed charge density of Q_f=-4x10^{12} cm^{-2} in the Al_2O_3, which is consistent with results published earlier by other authors. The apparent rise in Q_f for very thin Al_2O_3 films might be due to calibration errors for ultrathin Al_2O_3 films during the Corona charge experiment. The total amount of deposited Corona charge, as well as the dielectric constant ε, are determined by calibrating the increase in deposited Corona charge on a sample of known ε and measuring the change of surface potential of the Al_2O_3 layer with a Kelvin probe. However, leakage currents might start to play a role for ultrathin Al_2O_3 films, reducing the total amount of Corona charge remaining on the sample surface. Consequently, the fixed charge density Q_f in the ultrathin films is expected to be closer to the lower bound of the error margin. Taking this into consideration, we find the same high negative fixed charge density of Q_f=-4x10^{12} cm^{-2} for all samples from 1 nm to 32 nm thickness, which indicates that the negative charges are located within 1 nm of the interface.
Consequently, even ultrathin Al2O3 films of 1 nm thickness profit from the high level of field-effect passivation, enabling surface recombination velocities S_{eff}<100cm/s at $\Delta n=10^{15}$ cm^{-3}on these samples.

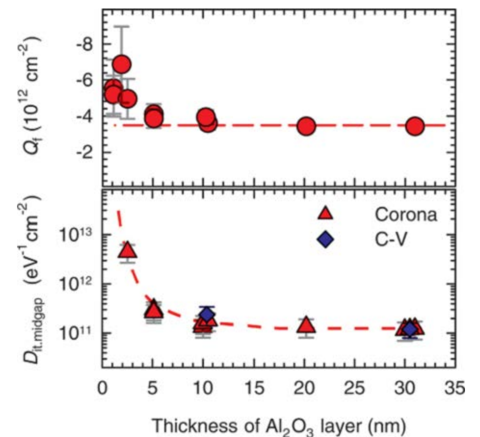

Figure 3: Fixed charge density Q_f (top graph) and midgap interface state density $D_{it,midgap}$ (bottom graph) as determined by Corona charge analysis (red symbols) and capacitance – voltage analysis (blue diamonds) of Al2O3 films deposited by plasma-assisted ALD. The dashed lines are guides to the eye.

In summary, it was shown that the ALD processes, which are compatible with industry demands, reveal passivation layers with excellent properties suitable for future generations of high-efficiency silicon solar cells. Further details the can be found at J. Appl. Phys. 109, 113701 (2011).

ACKNOWLEDGMENTS
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