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Investigation of crystalline silicon surface passivation by positively charged PO_x/Al_2O_3 stacks

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ABSTRACT

We investigate the passivation of crystalline Si (c-Si) surfaces by phosphorus oxide (PO_x) thin films deposited in an atomic layer deposition (ALD) reactor and capped in-situ by ALD Al_2O_3. Passivation is demonstrated on both *n*- and *p*-type (100) Si surfaces, and for PO_x/Al_2O_3 stacks deposited at both 25 °C and 100 °C. In contrast to Al_2O_3 alone, PO_x/Al_2O_3 passivation is activated already by annealing at temperatures as low as 250 °C in N_2 in all cases. Best results were obtained after annealing at 350 °C and 450 °C for films deposited at 25 °C and 100 °C respectively, with similar implied open-circuit voltages of 723 and 724 mV on *n*-type (100) Si. In the latter case an outstandingly low surface recombination velocity of 1.7 cm/s and saturation current density of 3.3 fA/cm^2 were obtained on 1.35 Ω cm material. Passivation of *p*-type Si appeared somewhat poorer, with surface recombination velocity of 13 cm/s on 2.54 Ω cm substrates. Passivation was found to be independent of PO_x film thickness for films of 4 nm and above, and was observed to be stable during prolonged annealing up to 500 °C. This excellent passivation performance on *n*-type Si is attributed partly to an unusually large *positive* fixed charge in the range of 3–5 × 10^{12} cm^{-2} (determined from capacitance–voltage measurements) for stacks deposited at both temperatures, which is significantly larger than that exhibited by existing positively charged passivation materials such as SiN_x. Indeed, passivation performance on *n*-type silicon is shown to compare favourably to state-of-the-art results reported for PECVD SiN_x. PO_x/Al_2O_3 stacks thus represent a highly effective positively charged passivation scheme for c-Si, with potential for *n*-type surface passivation and selective doping applications.

1. Introduction

Effective surface passivation has long been understood to be essential to realizing high-efficiency crystalline silicon (c-Si) solar cells, and has therefore been an important focus of research for many years. Although the materials and methods discovered thus far already enable outstanding passivation of c-Si surfaces, the exploration of new passivating materials remains of interest because these can have properties which make them advantageous for specific applications. This is especially the case as the range of functions a passivation layer is expected to perform continues to expand (particularly with the current interest in passivating contacts). Additionally, by understanding how different materials achieve passivation we deepen our understanding of passivation mechanisms in general.

In the last decade the list of materials known to be capable of passivating c-Si has expanded from the well-established Si-based compounds (SiO_2, SiN_x, and a-Si:H) to embrace a wide variety of newer materials [1], including Al_2O_3 [2], AlN [3], Ga_2O_3 [4], TiO_2 [5], Ta_2O_5 [6], HfO_2 [7], Nb_2O_5 [8], and ZnO [9]. Most of these new materials are metal oxides, and most feature a negative fixed charge at their interface with Si which makes them well-suited to passivating *p*-type Si surfaces, but less well-suited to passivating *n*-type surfaces. For the latter task SiN_x deposited by plasma-enhanced chemical vapour deposition (PECVD) [10], which has been known since the 1980s, remains the preferred solution, due partly to its relatively large positive charge, which has remained unmatched by newer passivation materials.

We have recently demonstrated unprecedentedly effective passivation of InP surfaces using a non-metal oxide, namely phosphorus oxide (PO_x), capped by Al_2O_3 [11]. In this structure, the Al_2O_3 capping layer acts as a moisture barrier to provide chemical stability to the PO_x, which is known to be highly hygroscopic, and therefore unstable when exposed to atmospheric moisture (uncapped PO_x films were observed to undergo rapid visible degradation on exposure to atmosphere). These PO_x films are amorphous and highly transparent, with a wide bandgap (> 5 eV) and a refractive index of 1.66–1.67 at 632 nm, which makes them well-suited to solar cell applications.

As we have recently reported [12], such PO_x/Al_2O_3 stacks can also provide highly effective surface passivation of c-Si. In particular, they

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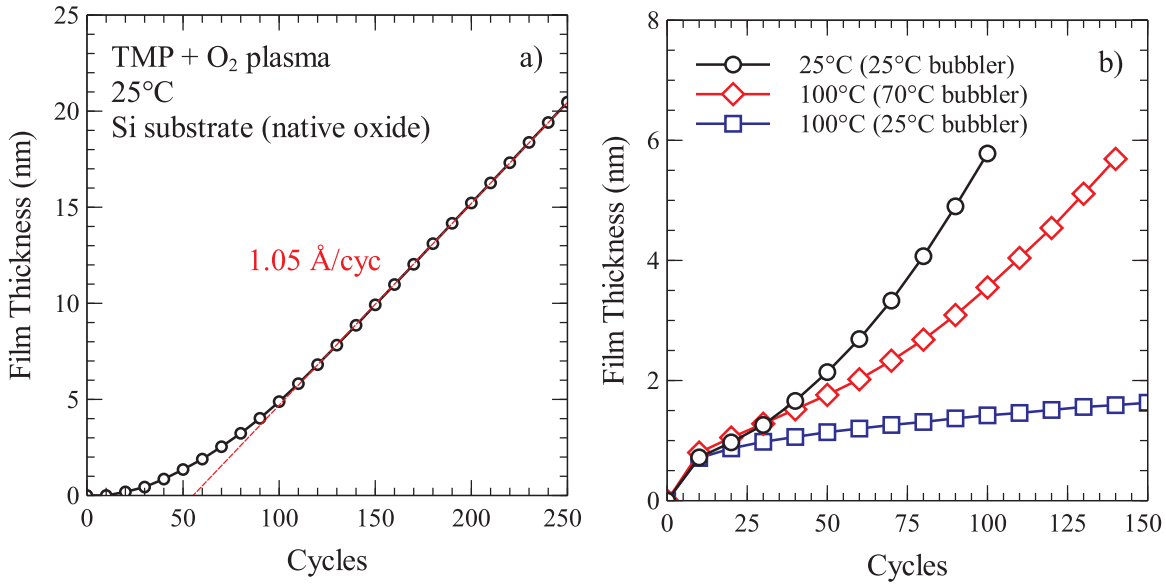

Fig. 1. Film thickness vs number of deposition cycles for PO_x films deposited a) at 25 °C on a polished (100) Si substrate with a native oxide (25 °C bubbler temperature), and b) at 25 or 100 °C on HF-etched, polished (100) Si substrates (for bubbler temperatures of 25 °C and 70 °C). The TMP dose time was 500 ms in all cases (with a 10 s hold step).

provide outstanding passivation of *n*-type surfaces due to their unusually large positive charge. In this work we explore the passivation of these stacks in more detail. We report passivation results for PO_x/Al_2O_3 deposited at both 25 and 100 °C, and on both *n*- and *p*-type Si, and examine the influence of PO_x film thickness and annealing time. We show that PO_x/Al_2O_3 occupies a unique position among existing passivation schemes due to its unmatched positive charge, and compare PO_x/Al_2O_3 passivation performance to state-of-the-art results for PECVD SiN_x.

2. Experimental details

PO_x films were deposited at temperatures of 25 and 100 °C in an Oxford Instruments FlexAL atomic layer deposition (ALD) reactor by exposing samples alternately to trimethyl phosphate (TMP, $(CH_3)_3PO_4$) and an O_2 plasma in a cyclic fashion, with separating Ar purges. Fig. 1a shows the resulting PO_x film thickness measured by in-situ spectroscopic ellipsometry as a function of the number of cycles at 25 °C, which exhibited a linear behaviour following an initial nucleation delay when deposited on Si surfaces with a native oxide (similar behaviour was observed at 100 °C). The steady-state growth-per-cycle (GPC) was not observed to saturate with respect to the TMP dose time, so that this process should be considered as pulsed chemical vapour deposition rather than ALD. On HF-etched surfaces the growth of a thin (~1 nm) interfacial oxide due to O_2 plasma exposure was apparent in the first cycles (Fig. 1b), after which deposition proceeded as on surfaces with a native oxide. ALD Al_2O_3 capping layers were deposited in-situ at the same temperature from trimethyl aluminium (TMA, $Al(CH_3)_3$) and O_2 plasma. The deposited film thickness was 5–6 nm for the PO_x and 14–15 nm for the Al_2O_3, unless stated otherwise.

Symmetric lifetime test structures with PO_x/Al_2O_3 stacks (where the PO_x was deposited first) or Al_2O_3 only were fabricated on 280 µm thick double-side-polished float-zone (100) 1–5 Ω cm *n*- and *p*-type Si wafers, which received a standard RCA clean and HF dip immediately prior to PO_x/Al_2O_3 or Al_2O_3 deposition. Post-deposition annealing was performed in a Jipelec rapid thermal processing system in N_2. Lifetime measurements were performed using a Sinton WCT 120TS photoconductance lifetime tester. The surface saturation current density J_{0s} was determined using the method of Kane and Swanson [13], assuming an intrinsic bulk lifetime given by the model of Richter et al. [14] and an intrinsic carrier concentration $n_i = 8.6 \times 10^9$ cm^{-3} (from the expression of [15] at 25 °C). The upper limit of the effective surface recombination velocity $S_{eff,UL}$ was calculated using the same intrinsic lifetime model [14].

3. Results and discussion

Fig. 2a shows the measured effective excess carrier lifetime τ_{eff} at an excess carrier concentration Δn of 10^{15} cm^{-3} as a function of post-deposition annealing temperature for *n*-type wafers passivated by PO_x/Al_2O_3 stacks or Al_2O_3 films deposited at 25 °C, and annealed consecutively at a series of increasing temperatures for 10 min in N_2. A deposition temperature of 25 °C was chosen for the initial investigations because it is the same as that previously used in the case of InP [1]. The initial lifetime results are quite encouraging, with a peak lifetime of 1.9 ms obtained for the PO_x/Al_2O_3-passivated sample after annealing at 350 °C, corresponding to $S_{eff,UL}$ of 6.8 cm/s. Perhaps more strikingly, the passivation of the PO_x/Al_2O_3 stacks appears to be activated at significantly lower annealing temperatures than in the case of Al_2O_3, with a lifetime of 1.2 ms obtained already after annealing at 250 °C. This clearly shows that the observed passivation is not simply due to the Al_2O_3 capping layer, and suggests that the Si–PO_x surface passivation kinetics are fundamentally dissimilar from those of Si–Al_2O_3.

Closer examination of the injection-dependent lifetime data (Fig. 2b) reveals significant changes in lifetime injection dependence with annealing. The lifetime after annealing at 250 °C is well-described by a single-diode model, with a surface saturation current density J_{0s} of 49 fA/cm^2 per side, suggesting that the surface is strongly accumulated or inverted due to charge in the dielectric stack. Following annealing at higher temperatures the lifetime simultaneously increases in high injection, while decreasing in low injection, such that the surface recombination can no longer be adequately parameterized by J_{0s}. The reason for this is not clear, but may be related to the large hysteresis observed in capacitance–voltage measurements of the same stacks, as discussed later. Interestingly however, the lifetime measured after annealing at 350 °C approaches very close to the intrinsic limit in high injection, which is reflected in an exceptionally high 1-Sun implied open-circuit voltage of 723 mV at 25 °C, and already indicates the exceptional passivation potential of these stacks.

Even better passivation results were obtained for PO_x/Al_2O_3 stacks