Solar Energy Materials & Solar Cells 142 (2015) 42–46

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Passivation of c-Si surfaces by ALD tantalum oxide capped with PECVD silicon nitride

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ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form
21 May 2015
Accepted 22 May 2015
Available online 16 June 2015

Keywords:
Surface passivation
Tantalum oxide
Silicon nitride
Solar cells

ABSTRACT

We demonstrate effective passivation of a variety of crystalline silicon (c-Si) surfaces by thermal atomic layer deposited (ALD) tantalum oxide (Ta_2O_5) underneath a capping silicon nitride (SiN_x) layer by plasma enhanced chemical vapor deposited (PECVD). Surface recombination is investigated as a function of Ta_2O_5 thickness for *p*- and *n*-type Si substrates, both with and without boron (p^+) or phosphorus (n^+) diffusions. It is found that the recombination decreases markedly with increasing Ta_2O_5 thickness on *p*, *n* and p^+ c-Si surfaces, but it follows an opposite trend on n^+ c-Si surfaces. In all four cases, the surface recombination velocity plateaus at a Ta_2O_5 thickness of 12 nm. The thermal stability of surface passivation by Ta_2O_5/SiN_x is examined by subjecting p^+ and n^+ diffused wafers to a typical solar cell metallization firing process, finding that it is essentially stable on p^+ diffusions, but not on n^+ ones, regardless of Ta_2O_5 thickness. We also evaluate the passivating properties of the Ta_2O_5/SiN_x stack on planar {100}, planar {111}, and textured *n*-type undiffused silicon surfaces, finding that (i) planar {111} Si exhibits a 4.6-fold higher recombination than planar {100} Si, and (ii) recombination at a textured surface is approximately equivalent to that at a planar {111} after surface area correction. Furthermore, the area-corrected recombination ratio of textured to planar {100} boron diffused p^+ regions is shown to be 2.2 for three different diffusions with sheet resistances at 56, 122, and 214 Ω/sq. Finally, optical simulation reveals a low reflection and negligible absorption loss for the Ta_2O_5/SiN_x stack. The Ta_2O_5/SiN_x stack is thus demonstrated to be an excellent surface passivation and antireflection coating for high efficiency silicon solar cells.

1. Introduction

In recent years double-side passivated silicon solar cells are finding widespread acceptance in photovoltaic pilot and production lines, thanks to the continuous improvement in surface passivation of *p*-type crystalline silicon (c-Si). One of the key requirements in passivating effectively the *p*-type surfaces is a high density of negative insulator charge, which produces a high concentration of majority holes, and consequently a low concentration of minority electrons at the c-Si surface. The highly negative charged dielectrics in conjunction with a low interface defect density is of high interest to silicon photovoltaics in (i) overcoming efficiency limitations imposed by the use of conventional Al-alloyed back surface on *p*-type silicon solar cells, and (ii) enabling the transferal to *n*-type silicon cells with its concomitant advantages [1]. Aluminum oxide (Al_2O_3) is the best-established negatively charged dielectric ($\sim 10^{12}$–10^{13} cm^{-2}), and is commonly used to passivate *p*-type silicon in photovoltaic laboratories and industry [2–4]. Nevertheless, several other dielectrics including titanium oxide [5,6], aluminum nitride [7], hafnium oxide [8] and gallium oxide [9], also possess a negative charge and have been reported to provide a reasonable level of surface passivation.

Recently, we have found a high level of surface passivation by another negatively charged dielectric—tantalum oxide (Ta_2O_5) [10]. By capping a 12 nm thick Ta_2O_5 prepared by atomic layer deposition (ALD) with a 85 nm silicon nitride (SiN_x) layer prepared by plasma enhanced chemical vapor deposition (PECVD), we obtained a low surface recombination velocity (< 5 cm/s) on low-resistivity (≤ 1.0 Ω cm) *p*-type and *n*-type c-Si wafers. As revealed by capacitance–voltage measurements in Ref. [10], a negative fixed insulator charge density of -1.8×10^{12} cm^{-2} was found in the uncapped Ta_2O_5 films, and -1.0×10^{12} cm^{-2} in the Ta_2O_5/SiN_x stack. Given the possible beneficial effect of a negative charge was weakened upon SiN_x capping, the substantial improvement in surface passivation after SiN_x capping can be primarily attributed to a reduction in the defect density at the Ta_2O_5/c-Si interface, presumably via hydrogenation during SiN_x deposition.

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http://dx.doi.org/10.1016/j.solmat.2015.05.032
0927-0248/

Furthermore, Ta_2O_5 also has an excellent optical properties, with a relatively high refractive index and a negligible absorption of the visible sunlight [11], making it a promising dielectric for photovoltaic applications, both as a passivating and antireflection coating (ARC) layer. In this contribution, we further explore such applications by examining the effect of Ta_2O_5 thickness on the recombination rate at several types of c-Si surfaces, including *p*-type and *n*-type undiffused, boron-diffused p^+, and phosphorus-diffused n^+. We also examine the effect of crystal orientation and surface morphology on the recombination rate, including planar {100}, planar {111}, and textured silicon with random upright pyramids. Finally, the optical properties of Ta_2O_5 are measured and the antireflection performance of Ta_2O_5/SiN_x stacks is simulated.

2. Experimental details

Lifetime samples for Section 3.1 were fabricated on 0.8 Ω cm *p*-type and 1.0 Ω cm *n*-type, {100} float-zoned (FZ) low-resistivity c-Si wafers with a thickness of 275 and 390 μm, respectively; and phosphorus diffused (n^+) 100 Ω cm *p*-type and boron diffused (p^+) 100 Ω cm *n*-type FZ high-resistivity c-Si wafers with a thickness of 390 and 280 μm, respectively. The undiffused wafers were etched in tetramethylammonium hydroxide (TMAH, 25 wt%) at ~85 °C to remove saw damage. Phosphorus and boron diffusions were performed in quartz tube furnaces using liquid $POCl_3$ and BBr_3 sources, resulting in sheet resistances of 120 ± 5 Ω/sq for both diffusions as measured by four-point probe.

Besides the same 1.0 Ω cm *n*-type, {100}-oriented wafers used in Section 3.1, lifetime samples for Section 3.2 also includes (i) {111}-oriented planar *n*-type FZ silicon wafers with a resistivity of 1.0 Ω cm and a thickness of 290 μm, and (ii) textured silicon wafers with random upright pyramids, which were prepared by immersing the as-cut 1.0 Ω cm *n*-type, {100} samples in an alkaline solution of TMAH, deionized water, isopropyl alcohol (IPA) and dissolved silicon at a temperature of 85 °C for 60 min [12–16]. In addition, Section 3.2 also includes planar and random pyramidally textured boron-diffused samples with three different sheet resistances of 56, 122, and 214 Ω/sq.

All samples were cleaned by the RCA (Radio Corporation of America) procedure and dipped in HF to remove any remaining oxide prior to Ta_2O_5 deposition. The Ta_2O_5 films were prepared by a thermal ALD system (R200 Advanced, Picosun) using Tantalum Ethoxide as tantalum precursor, H_2O as the oxidant, and N_2 as the purge gas. The deposition temperature was 250 °C, and the deposition rate was determined to be 0.3 Å/cycle by ex-situ spectroscopic ellipsometry (J.A. Woolam M2000 ellipsometer). The film thickness and wavelength-dependent refractive index *n* and absorption coefficient α were determined by fitting polarized reflectance using the Tauc–Lorentz model [17]. Deposition cycles were varied to obtain a series of thickness ranging from 3 to 24 nm. The capping SiN_x layers were prepared by a microwave/radio-frequency PECVD reactor (AK400, Roth & Rau). A detailed description of the reactor and deposition conditions is given elsewhere [18]. The capping SiN_x has a thickness of 85 nm and a refractive index of 1.93 at 632 nm.

The effective excess carrier lifetime τ_{eff} as a function of excess carrier density Δn was measured using a Sinton Instruments WCT-120 photoconductance tool [19]. Neglecting Shockley–Read–Hall recombination in the bulk of the wafer, the upper limit of the effective surface recombination velocity $S_{eff,UL}$ was calculated according to

$$S_{eff,UL} = \frac{W}{2}\left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{intrinsic}}\right), \quad (1)$$

where *W* is the Si substrate thickness and $\tau_{intrinsic}$ is the intrinsic bulk lifetime in Si parameterized by Richter et al. [20]. For the heavily diffused p^+ and n^+ Si samples, the recombination current density J_0 is extracted from the lifetime measurement by employing the technique developed by Kane and Swanson [21] with an intrinsic carrier concentration $n_i = 8.6 \times 10^9\ cm^{-3}$ at 25 °C. The lifetime measurements were conducted in transient mode, leading to an independence of optical factor on determination of J_0.

3. Results and discussion

3.1. Effect of Ta_2O_5 thickness on surface recombination

Fig. 1(a) depicts the passivation quality provided by as-deposited Ta_2O_5 and SiN_x-capped Ta_2O_5 films on *p*- and *n*-type undiffused c-Si samples for a range of Ta_2O_5 thicknesses. As can be seen, the as-deposited Ta_2O_5 films provide a poor surface passivation on both *p*- and *n*-type wafers with $S_{eff,UL}$ greater than 500 cm/s, regardless of the Ta_2O_5 thickness. Note that the passivation could not be improved by thermal annealing in 5% H_2 forming gas at temperatures between 250 and 450 °C. By contrast, upon capping the ALD Ta_2O_5 with a PECVD SiN_x layer, the level of surface passivation is significantly improved and exhibits a strong dependence on Ta_2O_5 thickness. As the Ta_2O_5 thickness increases, $S_{eff,UL}$ on both *p*- and *n*-type wafers first decreases, and then tends to saturate when the Ta_2O_5 thickness exceeds 12 nm. The lowest $S_{eff,UL}$ we obtained is 5.0 cm/s and 3.2 cm/s at $\Delta n = 10^{15}\ cm^{-3}$ on *p*-type and *n*-type c-Si wafers, respectively.

The passivation provided by the Ta_2O_5/SiN_x stack on boron-diffused p^+ wafers is also found to be excellent. Fig. 2 plots the recombination current density J_0 as a function of Ta_2O_5 thickness for boron-diffused p^+ and phosphorus-diffused n^+ regions. For reference, the J_0 for ALD Al_2O_3-passivated p^+ and PECVD SiN_x-passivated n^+ are also included as dashed lines. The deposition details of ALD Al_2O_3 can be found in Ref. [22]. The passivating SiN_x was deposited using the same process parameters as those for the capping SiN_x. Note that the as-deposited Ta_2O_5 without SiN_x capping provides little passivation on the diffused samples (not shown in Fig. 2). As can be seen, the Ta_2O_5/SiN_x stack provides a high level of surface passivation of p^+ surfaces,

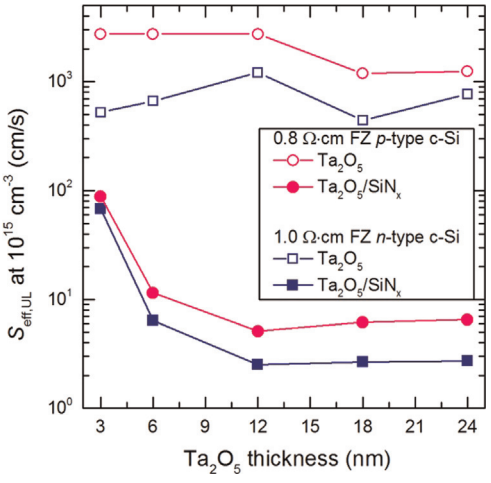

Fig. 1. The upper limit to surface recombination velocity $S_{eff,UL}$ at $\Delta n = 10^{15}\ cm^{-3}$ as a function of the Ta_2O_5 thickness on 0.8 Ω cm *p*-type and 1.0 Ω cm *n*-type Si wafers when passivated by Ta_2O_5 films and Ta_2O_5/SiN_x stacks.