Deposition pressure dependent structural and optoelectronic properties of ex-situ boron-doped poly-Si/SiO\textsubscript{x} passivating contacts based on sputtered silicon

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\begin{abstract}
Among common methods to form polycrystalline silicon (poly-Si) films for passivating-contact solar cells, physical vapor deposition, in particular sputtering, is the safest one as it does not require any toxic gaseous precursors. One of the critical parameters to control the properties of sputtered silicon films is their deposition pressure. In this work, structural and optoelectronic characteristics of ex-situ boron-doped poly-Si/SiO\textsubscript{x} passivating contacts, formed from sputtered intrinsic amorphous silicon (a-Si) deposited at different pressures on top of SiO\textsubscript{x}/c-Si substrates and subjected to a high-temperature boron diffusion step, are investigated. The deposition rate and density of the as-deposited a-Si films increase with reducing pressure. Low-temperature photoluminescence spectra captured from the as-deposited samples at different pressures do not show typical emissions from hydrogenated a-Si. Meanwhile, their Fourier-transform infrared absorption spectra all show Si–H stretching modes, indicating that hydrogen had been initially incorporated into the chemical SiO\textsubscript{x} layers and eventually hydrogenated the a-Si/SiO\textsubscript{x} interfaces during the sputtering process. After the high-temperature boron-diffusion step, all hydrogen-related peaks disappear. Lower pressure films (1.5 and 2.5 mTorr) show more consistent improved performance after hydrogen treatments, compared to higher pressure films (4 and 5 mTorr). The resultant passivating contacts at 2.5 mTorr achieve a low single-side recombination current density \( J_0 \approx 9 \) fA/cm\textsuperscript{2}, whereas their contact resistivity is still low at 15 m\( \Omega \)cm\textsuperscript{2}.
\end{abstract}

1. Introduction

Passivating-contacts based on a layer of doped polycrystalline silicon (poly-Si) and an ultra-thin interfacial silicon oxide (SiO\textsubscript{x}) layer on top of a crystalline Si (c-Si) substrate have been shown to be able to overcome the efficiency limitations of the current aluminium back surface field (Al-BSF) and passivated emitter and rear contact (PERC) industrial solar cell technologies. Several groups have demonstrated laboratory efficiencies of \( \geq 24\% \)\textsuperscript{[1–4]} for solar cells with poly-Si passivating contacts. There are many approaches to form the poly-Si film, and they can broadly be classified in two categories, chemical vapor deposition (CVD) and physical vapor deposition (PVD). In the CVD methods, the poly-Si films are obtained by recrystallizing amorphous Si (a-Si) layers deposited by plasma-enhanced CVD (PECVD)\textsuperscript{[2]}, low-pressure CVD (LPCVD)\textsuperscript{[5–7]}, atmospheric pressure CVD (APCVD)\textsuperscript{[8]}, or hot-wire CVD (HWCDV)\textsuperscript{[9]}. Meanwhile, the PVD method, specifically sputtering, has been used widely in microelectronics, optics and coatings of thin films\textsuperscript{[10]}. In PV, it is often used to deposit thin-film absorbers for CdTe\textsuperscript{[11]} and CIGS\textsuperscript{[12]} solar cells, transparent conductive oxide (TCO)\textsuperscript{[13]} solar cells, transport conductive oxide (TCO)\textsuperscript{[13]} and intrinsic a-Si films for heterojunction Si solar cells\textsuperscript{[14]}, and indium zinc oxide (IZO, one type of TCO) for perovskite solar cells\textsuperscript{[15]}

One of the most important parameters to control the properties of a-Si films deposited by sputtering is the deposition pressure. In previous work\textsuperscript{[16]}, we have shown that with a fixed deposition radio frequency...
(RF) power density of a Si target and varying power densities of a co-doped boron target, the total dose of boron in the films can be controlled. Although we were successful in demonstrating a good efficiency of 23.7% on the finished devices [16], the effects of sputtering conditions and doping process happened concurrently, yielding difficulties in understanding their individual impacts on the contact performance. In this study, we investigate a hole-selective contact formed by sputtering intrinsic a-Si onto a SiO\textsubscript{2}/c-Si substrate and performing ex-situ boron diffusion in a high-temperature furnace. In this way, we can separate the effects of the a-Si deposition pressure from the doping process, and investigate the impacts of the as-deposited intrinsic Si film properties on their final passivating contact performance. The effects of the deposition pressure on structural, optoelectronic, and passivation properties of the poly-Si/SiO\textsubscript{2} contacts are studied by a combination of various characterization techniques. Once fully understood, these findings can be employed to fabricate high-quality passivating contacts via the sputtering methods.

2. Results and discussions

First, we investigate the effects of deposition pressure on the deposition rate of initial a-Si films. The thickness is measured by an ellipsometer and the deposition rate is calculated by dividing the thickness over a fixed deposition time of 30 min, as shown in Fig. 1A. From the figure, increasing the deposition pressure decreases the deposition rate. This can be explained by the fact that, although at higher pressures the increasing Ar ion density and current in the plasma lead to a higher sputtering yield, the sputtered Si atoms will more likely return to the target by a collision with the Ar ions due to a large mass difference between them. Consequently, a higher deposition rate is achieved at a lower pressure. Additionally, the density of the sputtered a-Si film is also strongly affected by the deposition pressure. Lower pressures (i.e. closer to vacuum conditions) will likely yield denser films.

We then study optoelectronic properties of the as-sputtered a-Si films and subsequent passivating contacts. Fig. 1B shows photoluminescence (PL) spectra captured from the as-deposited a-Si/SiO\textsubscript{2}/c-Si samples at various pressures and a reference spectrum of a 50-nm PECVD a-Si:H/ SiO\textsubscript{2}/c-Si sample (pink color line), using a 405-nm excitation laser at 80 K. The PL spectrum from the reference sample shows a clear peak of hydrogenated a-Si (a-Si:H) located at ~1000 nm, confirming the existence of hydrogen inside the films. At 405-nm laser light is mostly absorbed in the a-Si layer (the penetration depth of UV light is typically in the order of a few nanometers). Fig. 1C shows the PL spectra from the samples after an 890 °C boron-diffusion step. The spectra show a clear sharp peak located at ~1125 nm, which is the c-Si band-to-band emission from the substrate [17]. Besides the c-Si peak, we observe another clear peak located at ~1160 nm attributed to the band-to-band emission from the p + diffused c-Si layer (underneath the SiO\textsubscript{2} layer). It is not emitted from the poly-Si film as it is still present after removing the poly-Si film. This peak shifts to longer wavelengths compared to the c-Si peak due to bandgap narrowing effects in heavily doped c-Si [23,24]. At ~1300–1600 nm, there are broad peaks which are reported in our previous work as emissions from radiative defects inside the poly-Si films [17].

Fig. 2A shows Fourier transform infrared (FTIR) absorbance spectra captured from the as-sputtered a-Si films. Surprisingly, there are Si–H stretching modes in the spectra, indicating the presence of hydrogen inside the samples. As the sputtering process does not involve any sources carrying hydrogen, the hydrogen should be mostly located at the a-Si/SiO\textsubscript{2} interfaces, not in the bulk of the a-Si films. The hydrogen could be incorporated into the SiO\textsubscript{2} film during the chemical oxide growth and then hydrogenate the first few nanometers of the sputtered a-Si films. From Fig. 2A, lower pressures form a larger fraction of monohydride Si–H\textsubscript{1} stretching mode (2000 cm\textsuperscript{-1}) compared to dihydride Si–H\textsubscript{2} stretching mode (2100 cm\textsuperscript{-1}) inside the sputtered a-Si films. At 4 mTorr (intermediate pressure), the two mode intensities are comparable and their ratio is similar to that of the PECVD a-Si:H film.

We can extract the total hydrogen content [H] using the absorbance spectrum at wavenumbers of 2000 cm\textsuperscript{-1} and 2100 cm\textsuperscript{-1} of Si–H\textsubscript{1} and Si–H\textsubscript{2}, respectively [25]. [H] can be estimated using the following equation [26]:

\[ [\text{H}] = A_{2000}I_{2000} + A_{2100}I_{2100}, \]

where \( I = \int (\alpha(\omega)/\omega) d\omega, \) \( \alpha \) is the wave-number dependent absorbance, and \( A \) is a calibration constant for each hydride mode. The calibration constant \( A \) is the same for the two hydride modes (2000 and 2100) and among samples with a similar measurement setup. Therefore, we can calculate a relative hydrogen concentration of [H]/A to compare among different deposition pressures using two Gaussian fits of the two peaks. The results are shown in the inset of Fig. 2A. As the sputtering pressure increases from 1.5 to 4 mTorr, the relative [H]/A inside the films increases. However, at 5 mTorr, it drops back to a similar level as that of the 1.5-mTorr case. In fact, there is interplay among the sputtered film thicknesses, densities and hydrogen amount. Therefore, we cannot conclude which deposition pressure will lead to a higher hydrogen concentration at the a-Si/SiO\textsubscript{2} interface, except the nature of the Si–H bonds (lower pressures yield more Si–H\textsubscript{1} and higher pressures yield more Si–H\textsubscript{2}). However, after the high-temperature diffusion (>800 °C) all the incorporated hydrogen has effused out, as demonstrated by the disappearance of the Si–H stretching modes in Fig. 2C.

In addition, changes in the Si–O absorption peak at 1100 cm\textsuperscript{-1} can

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**Fig. 1.** (A) Thickness and deposition rate of as-sputtered a-Si films on SiO\textsubscript{2}/c-Si substrates at various deposition pressures. (B) PL spectra from the as-sputtered a-Si films and a reference PECVD a-Si:H sample deposited at 300 °C with a thickness of ~50 nm. (C) PL spectra from the subsequent 890 °C boron-diffused poly-Si films. The PL measurements were conducted at 80 K with a 405-nm excitation laser.
also be observed [27,28]. For both the intrinsic a-Si and doped poly-Si cases, the highest deposition pressure (5 mTorr) yields the highest Si–O absorbance peak (Fig. 2B and D). Meanwhile, the other deposition pressures yield nearly identical peaks. At high pressures, impurities are more likely incorporated into the sputtered films. Therefore, the higher Si–O intensity could be due to the oxygen impurity incorporation. This could also partly explain the very low Si–H bond density at 5 mTorr (Fig. 2A) since Si–H bonds could be replaced by Si–O bonds.

We then investigate the crystallinity of the poly-Si films formed from sputtered a-Si at different pressures. Fig. 3A shows grazing incidence X-ray diffraction (GIXRD) spectra captured from the as-sputtered a-Si/SiO\textsubscript{x}/c-Si samples. For all samples investigated, only the peaks of Si (111) at 2\theta of 28.5° and Si (220) at 2\theta of 47.4° are consistently observed, confirming the polycrystalline nature of the films. The other two peaks of Si (311) at 2\theta of 56.0° and Si (400) at 2\theta of 69.4° are often convoluted with noise peaks from the XRD system (not shown here). We note that the intensities of the (111) and (200) peaks increase with reducing pressures. For Si, the penetration depth of the GIXRD system is ~1000 nm [29], which is well beyond the poly-Si film thickness (~50 nm). The SiO\textsubscript{x} layer can experience a break-up resulting in a higher dopant concentration in the near-surface region of the c-Si substrate. That leads to an increase in the GIXRD peak intensity as the increasing thickness of a-Si, and therefore poly-Si films, with reducing pressures.

Fig. 3B continues showing electrochemical capacitance voltage (ECV) profiles of electrically active boron in the doped poly-Si/SiO\textsubscript{x}/c-Si samples. The profiles show a similar average boron concentration of ~5–7x10\textsuperscript{20} cm\textsuperscript{-3} in the poly-Si bulk for all samples. The SiO\textsubscript{x} layer’s thickness can be estimated from Fig. 3B, representing the poly-Si film’s thickness (~20, 35, 50, and 60 nm for 5, 4, 2.5, and 1.5 mTorr, respectively). These thicknesses are much less than those of the as-sputtered a-Si films (Fig. 1A). Interestingly, although the poly-Si film at 1.5 mTorr is the thickest, the boron dopants are driven much more deeply into the c-Si substrate than those at other pressures, possibly due to differences in the film crystallinity and density, and/or in the oxide stoichiometric and thickness. At 1.5 mTorr, the sputtered Si atoms collide with the Ar ions the least, and hence could still remain a high kinetic energy when hitting the oxide surface. The impact could slightly reduce the oxide thickness and enhance the boron diffusion through the oxide. Also, it is likely that in the lowest pressure film, less boron atoms have been segregated in an electrically inactive form.

Fig. 3C compares transmission electron microscopy (TEM) images of the poly-Si/SiO\textsubscript{x}/c-Si samples formed by the initial sputtered a-Si films deposited at 1.5 mTorr and 5 mTorr. From the images, the poly-Si film thicknesses are ~60 nm and ~25 nm for the 1 mTorr and 5 mTorr samples, respectively, and similar to those obtained from the ECV profiles (Fig. 2B). Microscopic features of the poly-Si/SiO\textsubscript{x}/c-Si interfaces are displayed in the zoomed images in Fig. 3C. The SiO\textsubscript{x} layers are presented by thin stripes of amorphous phase, meanwhile the c-Si substrates are presented by uniform crystalline layers. A visual inspection on the poly-Si layers indicates that there is a larger fraction of the crystalline phase in the 1.5-mTorr sample than the 5-mTorr sample, similar to the GIXRD results. However, it is difficult to have a quantitative comparison from the TEM images due to the limited sample sizes.

Next, the contact resistivities of the passivating contacts are measured using the Cox and Strack method [30]. A test structure is illustrated as an inset in Fig. 3D. The contact resistivity is very low (~4 m\textOmega cm\textsuperscript{2} at 1.5 mTorr) and increases with increasing deposition pressures. Our previous work [16] has shown that, increasing the diffusion temperature will also decrease the contact resistivity. However, when the diffusion temperature is too high (~1000 °C or above), the oxide layer can experience a break-up resulting in a higher dopant concentration in the near-surface region of the c-Si substrate. That leads to an even a lower contact resistivity, but the surface passivation will be compromised. It is interesting to compare the results from this study to those of our earlier work on sputtered poly-Si/SiO\textsubscript{x} contacts [16], that is, between ex-situ and in-situ (co-sputtered) boron doping. The first thing to note is that for similar deposition pressure and final poly-Si film thickness the contact resistivity is very similar (~10 m\textOmega cm\textsuperscript{2} for 35–40
nm and 2.5–2.7 mTorr). It is also worth noting that, with relatively similar poly-Si film thicknesses but different deposition pressures the contact resistivity is ~2 orders of magnitude different (3.8 mΩ cm² with ~60 nm deposited at 1.5 mTorr in this work and 650 mΩ cm² with ~70 nm deposited at 2.7 mTorr in Yan et al.’s work [16]). Meanwhile, for similar pressures (2.5 mTorr in this work and 2.7 mTorr in Yan et al.’s work [16]), the contact resistivity varies with film thickness (~10 mΩ cm² for 35–40 nm and 650 mΩ cm² for ~70 nm). Therefore, both deposition pressure and film thickness strongly affect the final contact resistivity.

Fig. 3. (A) Grazing incidence X-ray diffraction (GIXRD) spectra and (B) electrically active boron profiles of 890 °C boron-diffused poly-Si/SiOₓ/c-Si samples at various pressures. Locations of the SiOₓ layers vary with thicknesses of the poly-Si films, as denoted by vertical lines in Fig. 2B. (C) Transmission electron microscopy (TEM) images of the poly-Si/SiOₓ/c-Si stacks at 1.5 and 5 mTorr. (D) Contact resistivities of the ex-situ boron doped poly-Si/SiOₓ passivating contacts. Reference ρc results from Yan et al. [16] for in-situ boron doped samples with the poly-Si layer thicknesses of ~40 and ~70 nm, sputtered at 2.7 mTorr and annealed at 900 °C, are also given.

Fig. 4. Recombination current density J₀ of different poly-Si samples diffused at 890 (A), 860 (B), and 830 (C) °C, with various a-Si deposition pressures, and before and after hydrogen treatments. The J₀ was measured using a quasi-steady state photoconductance (QSSPC) technique. Reference J₀ results from Yan et al. [16] for in-situ boron doped samples with the poly-Si layer thicknesses of ~40 and ~70 nm, sputtered at 2.7 mTorr and annealed at 800, 850 and 900 °C, are also given. The legends are the same for all figures.
Finally, we evaluate the passivating performance of these hole-selective contacts, represented by the recombination current density ($J_0$) parameter per side. Fig. 4 shows the $J_0$ results obtained from the samples after boron diffusion (as diffused), and after annealing in forming gas with and without an AlO$_x$H capping layer present (denoted as AlO$_x$H + FGA and FGA, respectively), at different diffusion temperatures (4A for 890 °C, 4B for 860 °C, and 4C for 830 °C). Results from our previous work [16] are also plotted in the figure to permit a comparison between the in-situ and ex-situ doping processes. Both show similar $J_0$ values at $\sim$2.5 mTorr (after FGA treatment in this work and $N_2$ annealing in Yan et al.’s work [16] for different temperatures). For samples deposited at 1.5–2.5 mTorr, the passivation quality increases after hydrogen treatments by AlO$_x$H + FGA, with the best $J_0$ of 9 fA/cm$^2$ (2.5 mTorr samples) which is even lower than our previous in-situ doping work (without AlO$_x$H + FGA) [16]. Meanwhile, samples with deposition pressures at 4 and 5 mTorr show inconsistent performance after the various hydrogen treatments. The results indicate that moving towards lower deposition pressures benefits the contact performance. However, it should be noted that the passivation quality of the poly-Si/SiO$_x$ stack also depends strongly on the poly-Si film thickness [3], which is another parameter that can be varied to achieve the best possible results.

3. Conclusions

In conclusion, we have reported the effects of sputtering pressure on the structural and optoelectronic properties of the as-deposited a-Si films and their corresponding ex-situ boron-doped poly-Si/SiO$_x$ passivating contacts. Lower pressures yield thicker and denser films with the same sputtering time, due to higher deposition rates. The PL spectra from the as-deposited films do not show the emissions that are typical of hydrogenated a-Si, confirming the absence of hydrogen in the sputtering process. The Si–H stretching modes observed by FTIR in the as-deposited films are likely a consequence of residual hydrogen incorporated to the oxide layer during its chemical growth. Nevertheless, such hydrogen signal disappears after the boron diffusion. The resultant poly-Si/SiO$_x$ contacts show a reasonably good initial passivation quality with $J_0$ of 24 fA/cm$^2$ at 2.5 mTorr, which improves to 9 fA/cm$^2$ after hydrogenation treatments.

3.1. Experimental section

Details of the sample preparation and experimental processes are described in Fig. 5. High-quality float-zone (FZ) (100) oriented, p-type c-Si wafers with a base resistivity of 85–115 Ω cm were used for all experiments. For the contact resistivity measurements by the Cox-Strack method [30], 200-μm thick, (100) oriented, 0.50–1 Ω cm p-type Czochralski (CZ) c-Si wafers were used. After saw damage etching and standard RCA cleaning steps, a thin layer of silicon oxide (SiO$_x$) was grown using a boiling nitric acid solution at 90 °C for 30 min. The resultant oxide thickness was $\sim$1.4 nm, measured by an ellipsometer. The samples were then transferred to the sputtering chamber and a layer of intrinsic a-Si was deposited on both sides of the wafers. A dual-magnetron, RF-biased AJA Sputter Coater system was used to sputter a-Si into the substrates. The RF power density of the silicon target was 3.1 W/cm$^2$. The deposition pressures were varied from 1.5 mTorr to 5 mTorr and all depositions were done in an Ar ambient for 30 min at room temperature. After the a-Si deposition, ex-situ boron diffusion doping was achieved using BBr$_3$ as a diffusion source in a quartz tube furnace. The diffusion was carried out at three different temperatures - 830 °C, 860 °C, and 890 °C - with the same deposition time of 25 min and driving time of 30 min. The resultant boron silica glass (BSG) layers after the diffusion were removed by dipping the samples in a diluted hydrofluoric acid (HF) solution. The forming gas (95%Ar and 5%H$_2$) annealing (FGA) was done at 400 °C for 30 min. A 40-nm layer of hydrogenated aluminium oxide (AlO$_x$:H) was deposited on both sides of the doped poly-Si samples and post annealed in FG to evaluate the performance of the passivating contacts after hydrogenation. All measurements were done after the AlO$_x$:H layers were removed (if present).

A HORIBA LabRAM system equipped with a confocal microscope was used for steady-state micro-PL spectroscopy measurements. A 405-nm laser was focused onto the sample surface through a 50× objective lens, yielding a spot diameter of 5 μm. An InGaAs detector with a detection range from 750 to 1600 nm was used to collect the emitted PL signal. All PL measurements were performed at $\sim$80 K using a liquid-nitrogen cooled THMS600 Linkam stage. A Sinton Instruments WCT-120 contactless photoconductance tester was used to perform injection-dependent recombination current density ($J_0$) measurement. The crystallinity of the poly-Si layers was analyzed by a grazing-incidence X-ray diffraction spectroscopy (GIXRD) method using a PANalytical X’Pert PRO MRD system with a Cu anode and an X-ray source wavelength $\lambda$ of 1.542 Å, at a fixed incidence angle of 1°.

Transmission electron microscope (TEM) phase contrast images were obtained using a FEI Tecnai F20 operated at 200 kV. The Fourier transform infrared (FTIR) absorbance spectra were recorded in the range of 400–4000 cm$^{-1}$ with a resolution of 6 cm$^{-1}$ by a Bruker VERTEX 80v vacuum spectrometer. The thickness measurements were done using a JA Woollam M2000D ellipsometer.

Declaration of competing interest

No known conflicts of interest.

CRediT authorship contribution statement

Andres Cuevas: Writing - review & editing. Daniel Macdonald: Supervision, Funding acquisition, Writing - review & editing. Hieu T. Nguyen: Conceptualization, Visualization, Writing - original draft, Validation, Supervision, Funding acquisition, Writing - review & editing.

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Appendix A. Supplementary data

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References


