Microstructure and Passivation Effects on Open Circuit Voltage in Low Temperature Deposited Silicon Thin Films

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ABSTRACT
Hydrogen-passivated silicon films grown via hot wire chemical vapor deposition (HWCVD) are promising candidates for polycrystalline Si solar cell absorber layers. We report on correlation of film microstructure and passivation with open-circuit voltage, a key cell electrical characteristic, for varying growth conditions and post-deposition treatments. We have examined the role of hydrogen-dilution on growth morphology and Voc, with results indicating sufficient hydrogen passivation in the ‘bulk’ of HWCVD-deposited Si films. Surface passivation is thus identified as the limiting factor in achieving higher Voc; hence we have examined the effectiveness of several post-deposition passivation treatments.

1. Objectives
Our goal is to elucidate the role of hydrogen in HWCVD Si film bulk passivation, crystalline fraction, growth morphology, and its relation to film electrical properties. Varying growth conditions and observing the subsequent effect on microstructure and open-circuit voltage enables us to optimize these characteristics for polycrystalline Si thin film solar cell absorber applications.

2. Technical Approach
Silicon films are grown on CZ-grown Si(100) via HWCVD, with either undoped or n-type with phosphine (5% in SiH₄) as the dopant gas, at substrate temperatures varying from 230 °C to 350 °C. Silane gas (1% in Ar) is diluted with hydrogen in various ratios:

\[ R = \frac{H₂}{SiH₄} \]

We used tungsten filaments operated at T~1700 °C to catalyze SiH₄ decomposition. Open circuit voltage measurements were performed for n-type films with phosphorus doping of \(1 \times 10^{15}\) cm\(^{-3}\) grown on CZ-grown p-type Si (100) with boron doping of \(1 \times 10^{16}\) cm\(^{-3}\). Steady-state \(V_{oc}\) measurements were performed on unmetallized HWCVD n-Si films/p-Si (100), and growth morphology was observed by cross-sectional transmission electron microscopy.

3. Results and Accomplishments
We have correlated hydrogen dilution with growth morphology and have used these observations to study the relationship between \(V_{oc}\) and microstructure.

3.1 Growth-Morphology
The structure of as a function of hydrogen dilution was investigated by electron microscopy, which reveals an increase in porosity for growth in the range \(230 °C < T < 350 °C\) as dilution is decreased from \(R = 480\) to \(R = 30\), for a total pressure of \(P = 120\) mTorr. The resulting images reveal a more rapid breakdown to a porous microstructure as \(R\) decreases, as shown in Fig. 1. The pore-permeated microstructure originates during film growth and pores are oriented perpendicular to the surface. Although films exhibiting this porous microstructure would be suspected to be prone to oxidation, Raman measurements taken after ambient exposure for ~10 weeks did not indicate oxide formation.

3.2 Open-Circuit Voltage
An increase in open-circuit voltage with hydrogen dilution is observed for 1000 nm thick films grown with a hydrogen dilution in the range \(0 < R < 244\) (Fig. 2). For \(R = 244\), an initial \(V_{oc}\) of 400 mV was observed, but \(V_{oc}\) decreased to 290 mV after one week of ambient exposure. Another set of films 885nm thick were grown with a hydrogen dilution ranging from \(45 < R < 180\), with a similar increase in \(V_{oc}\) observed with H-dilution. The highest stabilized \(V_{oc}\) of 350 mV was observed for 885 nm thick films deposited at \(R=90\). We attribute the higher \(V_{oc}\) to lower film porosity compared to films grown at lower dilution, which leads to less surface recombination due to the smaller surface area. As the thickness of the film increases, dense epitaxial growth is observed to transition into a...
porous microstructure. For this reason, we do not observe a maximum stabilized $V_{oc}$ for the thickest film.

The open-circuit voltage of both the 125 nm and 885 nm films was measured initially and after 1 week in ambient air, and significant changes are observed. The rise in $V_{oc}$ over time in ambient air indicates sufficient passivation of the bulk of the film due to high hydrogen content during growth. We attribute this change in $V_{oc}$ to a change in surface passivation during ambient oxidation, suggesting that hydrogen passivation of defects in the 'bulk' of the film is sufficient to prevent bulk recombination from limiting $V_{oc}$.

**Fig. 3** Open-circuit voltage with hydrogen dilution after various post-deposition treatments.

### 3.3 Surface Passivation

The results of various surface treatments are shown in Fig 3. Annealing at 900°C causes a dramatic decrease in $V_{oc}$ that we attribute to hydrogen evolution from the film. Chemical oxidation by liquid immersion in H$_2$O: H$_2$O$_2$: NH$_4$OH during an RCA II clean results $V_{oc}$ comparable to those for films that undergo ambient air oxidation.

**Fig. 3** Open-circuit voltage with hydrogen dilution after various post-deposition treatments.

### 4. Conclusions

We investigated the correlation between microstructure and surface passivation on $V_{oc}$ in low temperature HWCVD polycrystalline silicon thin films. Film porosity increases with decreasing hydrogen dilution for films grown under high hydrogen dilution. In general, epitaxial growth and low porosity correlate with higher $V_{oc}$. Results from post-deposition treatments show promising improvements in $V_{oc}$ with RCA oxidation. A decrease in $V_{oc}$ is seen after high temperature anneals, suggesting loss of bulk hydrogen passivation during high temperature annealing. These results clearly demonstrate the ability to achieve high $V_{oc}$ for well-passivated films, and future work will address achieving stable passivation for HWCVD Si polycrystalline films with high initial $V_{oc}$.

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