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EPITAXIAL CRYSTAL SILICON ABSORBER LAYERS AND SOLAR CELLS GROWN AT 1.8 MICRONS PER MINUTE

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ABSTRACT

We have grown device-quality epitaxial silicon thin films at growth rates up to 1.8 μm/min, using hot-wire chemical vapor deposition from silane at substrate temperatures below 750°C. At these rates, which are more than 30 times faster than those used by the amorphous and nanocrystalline Si industry, capital costs for large-scale solar cell production would be dramatically reduced, even for cell absorber layers up to 10 μm thick. We achieved high growth rates by optimizing the three key parameters: silane flow, depletion, and filament geometry, based on our model developed earlier. Hydrogen coverage of the filament surface likely limits silane decomposition and growth rate at high system pressures. No considerable deterioration in PV device performance is observed when grown at high rate, provided that the epitaxial growth is initiated at low rate. A simple mesa device structure (wafer/epi Si/a-Si(i)/a-Si:H(p)/ITO) with a 2.3-μm epitaxial silicon absorber layer was grown at 700 nm/min. The finished device had an open-circuit voltage of 0.424 V without hydrogenation treatment.

INTRODUCTION AND THE GROWTH RATE THEORY

Due to the potential to rapidly deposit high quality film silicon on inexpensive substrates coated with crystalline seed layers [1], hot wire chemical vapor deposition (HWCVD) of silicon shows great promise for cost-effective, large-scale production of film silicon photovoltaic devices by silicon epitaxy. Inexpensive substrates such as display glass or metallic foils [2-4], generally require absorber layer growth temperatures below 750°C. HWCVD epitaxy satisfies this requirement and thus can provide a means to circumvent the expensive processing steps used in wafer silicon technologies, where nearly one-half of module cost comes from the wafer itself.
To keep the capital costs of HWCVD epitaxy low, deposition rates must be high (of order micron/minute), without sacrificing the epitaxial silicon quality. High growth rates relax the requirements for light trapping by growing a thicker layer quickly, and can also allow creation of micron-scale surface texture by sacrificing part of the fast-grown, inexpensive absorber layer to etching.

Achieving fast epitaxial growth rates without compromising the layer quality can be challenging due to possibility of powder formation, higher defect concentration in the films, etc. Similarly, increasing the HWCVD growth rate itself can be done in various semi-empirical ways far from optimum conditions. Generally, the higher the silane molecular flux to the filament, the higher the growth rate. This flux, being proportional to the silane concentration in gas phase can be increased by the system pressure. However, the depletion of silane at low flow typically results in high hydrogen dilution and relatively low growth rate. On the other hand, increasing the silane flow leads to higher growth rate but poor silane utilization. In the present work, we examine and experimentally apply the optimized growth parameters (silane flow, system pressure, filament geometry) that lead to high epitaxial HWCVD growth rate, and reveal the rate-limiting factors. We base our approach on our earlier model for silicon epitaxy growth rate (GR) by Martin *et al.* [5] which quantitatively predicts GR values for wide range of silane flows into the HWCVD reactor, at moderate reactor pressures, and examine the limitaions that occur at higher pressures. The incoming silane decomposes on a hot W wire (filament) mostly into silicon atoms and hydrogen molecules, with relatively small and pressure-dependent fraction of atomic H [6]. The Si atoms then react with surrounding silane molecules to produce other simple radicals such as Si_2H_2, as well as higher silanes [6]. As long as the substrate temperature is above 650 ^oC, most radicals (both Si Si_2H_2) contribute to high quality epitaxial growth [5].

The deposition chemistry starts at the filament, and its geometry is critical for achieving high GR. Its surface area, A_{fil}, determines the rate of useful radical production, while the radical flux pattern away from it determines how many radicals impinge on the substrate. Under our typical HWCVD epitaxy conditions, the filament decomposes about 30% of the impinging silane, each outgoing Si atom reacts with SiH_4 to create Si_2H_2, all Si_2H_2 radicals travel to the substrate, and then, with the probability, $s \approx 1$, stick to it [5]. Martin *et al*. showed that the growth rate R_{rad} due to the radical flux from the filament is a product of silane flow, depletion, radical sticking coefficient, and a factor that accounts for filament geometry:

$$R_{rad} = G\left(\frac{1}{dL_{fil}}\right) \times f \times D\left(\frac{pA_{fil}\alpha}{f}\right) \times s \qquad (1)$$

where the units of R_{rad} are nm/minute. Here, G (nm/cm^3) is a geometrical factor that depends on the length of the filament L_{fil}, and on filament-substrate distance d because of radical conservation in the cylindrical flux pattern emanating from the wire filament [5]. Incoming silane flow is denoted by f. The silane depletion D defined by the relative decrease in the silane molecule concentration with filament on and off, $(n_{off} - n_{on})/n_{off}$ and is bound by $0 \le D \le 1$, where 1 represents the case where all silane is decomposed. Experimentally, this depletion of silane, D, is a function of f, system pressure p, and filament surface

area A_{fil}. Here, *f* and *p* control the quantity of new silane entering the chamber, and the dominant radical species impinging the substrate, respectively. The silane decomposition probability α is about 0.3 at low pressure [6]. Finally, *s* is the radical sticking probability to the growing surface, which for our epitaxial growth temperatures >650 C is constant and close to unity [5].
Thus, to increase growth rates one should: 1) decrease substrate-filament distance *d* and thereby increase the radical flux delivered to the substrate, 2) increase both silane flow *f* and system pressure *p* while maintaining a high depletion *D* of silane, 3) increase the filament area A_{fil} to increase the number of silane decomposition sites and thus depletion *D*.

In this work we detail how the total GR increases by implementing the high rate conditions 1-3. Our measurements show that the predicted *1/d* relationship for a cylindrical flux pattern holds except at very high pressures and small *d*, where the approximations break down. Moreover, at high *p*, the experimentally measured depletion decreases from the predicted value. These observations suggest that the reactions at the filament and gas phase chemistry very near the filament ultimately limit the *GR*, though we have not yet reached that limit. The absorber layer quality produced at high *GR* is comparable to absorber layers grown at low rates; our mesa structure devices with absorber layers deposited at 700 nm/min perform similarly to control devices with absorber layers grown at 50 nm/min.

EXPERIMENT

Epitaxial silicon films were grown on (100) oriented silicon wafers in HWCVD reactor. Before loading into the chamber, the surface oxide was stripped by bathing the wafer in dilute 4% HF for 30 seconds. Baseline pressures with filament on were below 10^{-6} Torr. After heating the wafer to about 750 ^{o}C, silane gas was flown into the reactor at a fixed flow *f*. We controlled the chamber pressure *p* over 2 – 100 mTorr range using a throttle valve on the turbo-pump. Silane gas was decomposed using a 0.5 mm diameter tungsten wire, wound 11 times ("standard filament") or 24 times ("compact filament") to make a coil with inner diameter of about 3 mm. We used 16 A current to heat the filament. The filament was attached to a translation arm allowing its distance to the substrate *d* to vary from 1 to 5 cm. The *GR* and material quality were determined by *in-situ* spectroscopic ellipsometry (SE). We measured *D* using a residual gas analyzer (RGA) attached to the chamber, by comparing the silane partial pressure during deposition to the silane partial pressure present with the filaments turned off.

To demonstrate the cell absorber layer quality in a high-growth rate epitaxial solar cell, we deposited a 2.3-μm epitaxial silicon absorber layer at 700 nm/min on a RCA-cleaned, (100) oriented, n^{+} (Si:As) silicon wafer. A mesa-isolated silicon heterojunction structure (wafer/epi-Si/a-Si(i)/a-Si:H(p)/ITO) was processed into the solar cell by wet and dry etching techniques [7]. We compared its performance against a control device with absorber layer deposited at 150 nm/min using our standard conditions of *f* = 20 sccm, *p* = 10 mTorr, *d* = 5 cm, and standard filament.

RESULTS AND DISCUSSION

Figure 1 demonstrates the total *GR* we achieved after implementing each of the three considerations detailed below Eq. 1. We first measured *s* by plotting the dependence of R_{rad} as function of product *f*D* following the approach of [5] and found that at these substrate temperatures, *s* ≈ 1 for all values of *f* and *p*. Deposition conditions for the leftmost data point of Fig. 1 represent our standard operating conditions (standard filament, 10 mTorr system pressure, 20 sccm silane flow). Here, the measured *GRs* of ~ 0.170 μm/min which is far below our estimated threshold *GR* of ~ 1 μm/min where module capital costs become largely *GR* independent for film c-Si PV. Under these standard conditions, silane depletion is moderate, (*D* = 0.78) indicating that about 22% of the silane leaves the system unreacted and therefore wasted. We now apply our three factors that lead to growth rate increse.

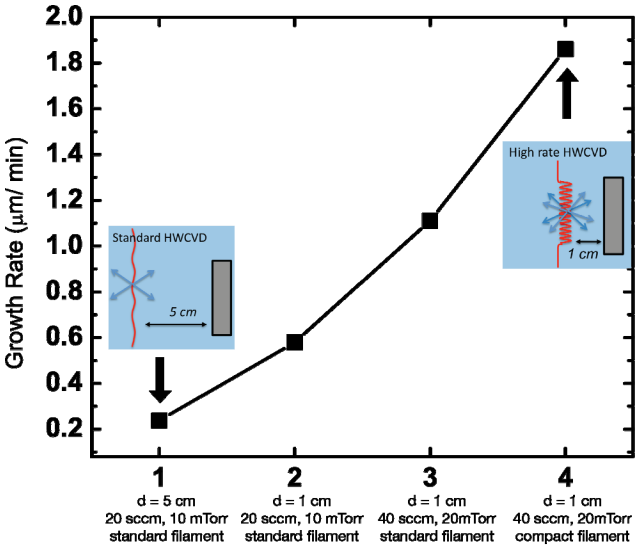

Figure 1. Growth rate for several experimental conditions. High rates are achieved left to right, by decreasing substrate-to-filament distance, increasing silane flow and pressure, and increasing filament area.

1) When we decrease *d* from 5 to 1 cm, while keeping all other parameters constant, *GR* more than doubles. The roughly 20 ^{o}C increase in substrate temperature due to the close proximity of the hot filament may slightly change *s* and the (small) contribution of thermal epitaxy, but this change is too small to account for the nearly 40% smaller *GR* as compared to factor 5 increase expected from just the radical flux geometry.

2) When *p* and *f* are both doubled from 10 mTorr to 20 mTorr and 20 sccm to 40 sccm (keeping *d* = 1cm) we achieve a *GR* of about 1.1 μm/min. Depletion *D* remained approximately unchanged, since the combined effects of doubling both *f* and *p* approximately cancel each other. We tried increasing *D* by increasing *p* further to 60 mTorr, but found that *D* actually decreased (Fig. 2), along with *GR* indicating a departure from the simple model predictions of Eq. 1.

3) The final increases in *GR* to 1.8 μm/min and above the target threshold of ~1 μm/min, were obtained by implementing the compact filament (upper right in Fig. 1). Also, a modest gain in *D* was obtained: the near doubling of A_{fil} increased *D* to 0.85, indicating that the near doubling of *GR* was most likely due to the additional filament length. Although we have demonstrated *GR* above the ~1 μm/min threshold, further increases in *GR* should be possible if we more deeply understand the physics limiting growth at small *d* and high *p.* In Fig. 2 the measured *GR* is plotted as function of *d*.

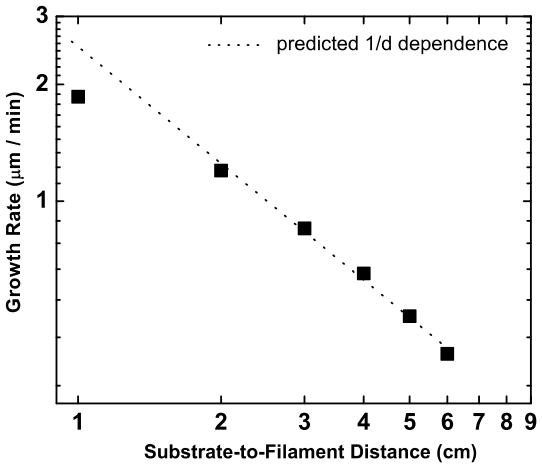

Figure 2. Growth rate versus substrate-to-filament distance for 40 sccm, 20 mTorr, and using the compact filament. Dotted line is the predicted 1/d dependence. The data deviate from the expected 1/d dependence (dotted line) for *d* < 2 cm.

At *d* > 2 cm*, GR* decreases according to *1/d* dependence expected for the cylindrical flux pattern emanating from the filament. [2]. Below *d* = 2 cm, we observe a departure from the 1/*d* dependence. This is likely due to the reduction in the number of collisions between the Si atoms from the filament and SiH_4. Several collisions are needed to initiate reaction between them to produce Si_2H_2. As the number of collisions drop with decreasing *d*, growth is likely due to Si atoms (1 Si into the film per SiH_4 decomposition on the filament) instead of Si_2H_2 (2 Si per decomposition), resulting in a 2X decrease in the growth rate. As mentioned above, at lower 10 mTorr pressure the decrease in *d* from 5 to 1cm lead only to doubling of the GR. At higher pressures, this effect becomes less pronounced as the number of collisions even at small *d* is relatively large. However, at still higher pressures above 40 mTorr (not shown) we observe an increase in the disilane partial pressure with the RGA, find silicon dust in the chamber after growth, and achieve no further increase in the growth rate. The optimal high growth rate conditions are therefore at small *d* and at pressures below the *p* at which higher silanes and particle form.

In conjunction with the formation of higher order silane radicals at high *p*, we also observe a decrease in the filament's ability to decompose silane. In Fig. 3, we plot *D* as *p* is increased while maintaining 20 sccm the flow at 20 sccm. At *p* < 40 mTorr, the data fit to the predicted value (dotted line, Ref. 5), but then deviate from the model prediction, to smaller values at higher pressures. This observation strongly indicates that a change occurs in the gas-filament interactions. Notably, the H_2 partial pressure is nearly 10X greater than the silane partial pressure for *p* > 40 mTorr (depletion around 0.8) and thus most of the high system pressure is due to molecular hydrogen. These hydrogens interact with filament surface (kept near 2100 ^oC), dissociate and temporarily bind to it [6] until recombining at with other bound H and leaving as hydrogen molecule. The large concentration of H bound to W filament surface might partially saturate the dissociation sites, which could affect the dissociation of incoming silane [8]. We are currently testing this hypothesis.

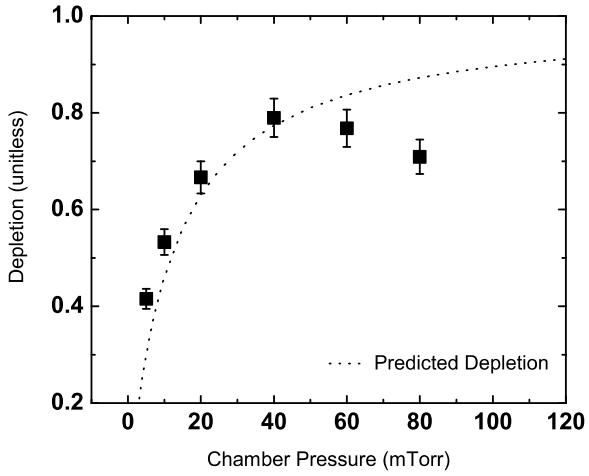

Figure 3. Depletion dependence on chamber pressure. The data deviate from the predicted depletion (dotted line) from pressure > 40 mTorr.

As a preliminary test of epitaxial Si quality, we deposited absorber layers for solar cells using the high rate conditions. The layer quality is highly sensitive to the initial moments of growth. When growth is initiated at high rates, the two-peak ε_2 SE signal at photon energy range 3 – 5eV shows a reduction from the strong wafer silicon peaks and never subsequently recovers to the wafer value; there are

also strong interference fringes in the near infrared region. This indicates polycrystalline silicon growth (confirmed by XRD) and a poor silicon-epitaxial silicon interface. We therefore adopted a slow-to-fast growth technique, whereby we initialize epitaxial growth at standard conditions (10 mTorr, 20 sccm, *d* = 5 cm) to obtain GR ~ 150 nm/min. The SE signal remains close to that of the Si wafer, suggesting good-quality starting epitaxial layer near the wafer interface. We then switch to high GR (for example 700 nm/min) at conditions of 20 mTorr, 40 sccm, and *d* = 2 cm.

Our preliminary results suggest the high rate absorber layer is of comparable quality to those layers grown under standard conditions. Table 1 shows the solar cell performance for devices with standard and high GR absorber layers, without hydrogen passivation. Here the absorber layers are epitaxial Si grown on heavily-doped "dead" n-type c-Si wafers.

Table 1. Comparison of standard and high rate solar cell performance.

Solar Cell	Growth Rate (nm/min)	V_{oc} (mV)	FF	Efficiency
Standard	**~150**	**470**	**63**	**3.1**
High Rate	**~700**	**420**	**61.7**	**2.2**

The high rate device has 50 mV less open circuit voltage, but has nearly the same fill factor as the standard device. These preliminary results give us confidence that high GR, high quality material is possible with some optimization of the growth conditions. These growth rates exceed by more than 10X those used in current a-Si:H and nc-Si:H manufacturing. Our highest epitaxial growth rates are nearly three times higher.

CONCLUSIONS

We have theoretically and experimentally examined the conditions necessary to obtain the high growth rate of the HWCVD epitaxial film silicon above ~ 1 micron/minute. By decreasing filament-substrate distance, maximizing silane flow and depletion product, and increasing the filament area we have achieved growth rate of 1.8 micron/minute. The device performance for high growth rate is comparable to that grown at low rate provided that the growth is initiated at low rate. The increase in growth rate at high system pressure is likely limited by high hydrogen concentration near and at the filament.

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