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High-Throughput Dry Processes for Large-Area Devices

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Printed October 1999**

High-Throughput Dry Processes for Large-Area Devices

LDRD FINAL REPORT

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ABSTRACT

In October 1996, an interdisciplinary team began a three-year LDRD project to study the plasma processes of reactive ion etching (RIE) and plasma-enhanced chemical vapor deposition (PECVD) on large-area silicon devices. The goal was to develop numerical models that could be used in a variety of applications for surface cleaning, selective etching, and thin-film deposition. Silicon solar cells were chosen as the experimental vehicle for this project because an innovative device design was identified that would benefit from immediate performance improvement using a combination of plasma etching and deposition processes. This report presents a summary of the technical accomplishments and conclusions of the team.

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EXECUTIVE SUMMARY

In October 1996, an interdisciplinary team began a three-year LDRD project to study the plasma processes of reactive ion etching (RIE) and plasma-enhanced chemical vapor deposition (PECVD) on large-area silicon devices. The goal was to develop numerical models that could be used in a variety of applications for surface cleaning, selective etching, and thin-film deposition. Silicon solar cells were chosen as the experimental vehicle for this project because an innovative device design was identified that would benefit from immediate performance improvement using a combination of plasma etching and deposition processes. The primary accomplishments of the team follow:

- Numerical models that closely predict the etch rate of Si in SF₆ plasmas were obtained, along with a fundamental understanding of which chemical species and reactions dominate the etching process.
- An analytical expression for the refractive index of deposited silicon nitride as a function of reaction parameters was obtained and used to deposit optimal films for best optical performance.
- A statistical multivariate analysis was performed to determine parameter sets for optimized electronic properties of deposited dielectric films on silicon surfaces.
- A relative improvement of 7 % in conversion efficiency of production-line solar cells compared to control cells was obtained.

These validated process models can be used in a variety of applications for surface cleaning, selective etching, and thin film deposition. The models will provide guidance for development of the next generation of plasma reactors and the development of new device designs and applications.

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INTRODUCTION

The goal of this work was to develop guidelines for high throughput dry processes that can effectively replace wet processes used in manufacturing of large-area devices and/or batches of moderate-area devices. Wet processes generally increase worker exposure to toxic and hazardous chemicals and tend to generate large volumes of liquid hazardous waste. Successful development of high throughput dry processing could eliminate much of the waste stream while minimizing worker exposure. This interdisciplinary project utilized Sandia's expertise in photovoltaics, plasma processing, sensor-based controls, and process modeling to develop more environmentally benign processes that can reduce costs and product realization times. Large-area commercial silicon solar cells were used as the test vehicle in this program. We developed a sequence of back end, dry processes for selective etching of the solar cell emitter, surface defect passivation, and deposition of the antireflection coating.

The use of large-area commercial solar cells was chosen as an experimental vehicle because plasma etching and deposition was seen as a means to improve the device performance with little increase in cost or waste stream. The most common commercial solar cells (normally 100-cm² or larger in area) are fabricated on either single-crystal- or multicrystalline-silicon (sc-Si or mc-Si, respectively). They typically use inexpensive screen printed metallization systems over a heavily doped emitter (to lower the contact resistance), and may be covered by a deposited antireflection coating like TiO₂. While the heavily doped emitter is required to reduce the contact resistance, it degrades the short wavelength response of the cell. The TiO₂ layer provides no surface passivation, which also reduces the short wavelength response. The performance of these cells could be significantly enhanced through a self-aligned, selective emitter etchback process combined with defect and surface passivation as illustrated schematically in Figure 1.

Figure 1. Schematic illustration of the self-aligned, selective emitter process used as the test vehicle in this project. The gridline is produced by firing a screen-printed silver paste. A dry etch process is used to etch back the heavy diffusion between the gridlines while the gridline protects the region beneath it. Finally, a nitride coating is deposited which provides both antireflection and surface passivation properties.

Removal of the upper part of the heavily doped emitter between the gridlines improves the short wavelength response by lowering the dopant concentration at the illuminated surface. A selective etchback procedure of this type would be most easily implemented if the gridlines could act as self-aligned masks for the underlying heavily doped silicon. This work utilized the unique capabilities of plasma processing to achieve this self-aligned, selective etch back process. A subsequent plasma-enhanced chemical vapor deposition (PECVD) process for silicon-nitride was used to deposit an antireflection coating and provide significant surface passivation for the etched-back emitter. The silicon-nitride was saturated with atomic hydrogen to better passivate the Si surface by exposing it to various amounts of ammonia-plasma during the course of its deposition.

FIRST-YEAR ACCOMPLISHMENTS

The project team performed an initial survey of available dry processing equipment including downstream etchers, batch plasma reactors, diode plasma reactors, and inductively coupled high-density plasma (ICP) reactors and selected our target reactors based on reactor availability at Sandia, compatibility with process chemistries, perceived process robustness, accessibility for diagnostics, degree of modeling complexity required, and reactor cost. These considerations led to the initial selection of the Vacutek Reactive Ion Etch (RIE) and Plasma-Enhanced Chemical Vapor Deposition (PECVD) tools located in the Compound Semiconductor Research Laboratory (CSRL). Empirical characterization of plasma etch and plasma CVD in these tools showed adequate performance and sufficiently low surface damage. A recent decision has been made to perform additional experiments in the Plasmatherm ICP tool (also in the CSRL) to investigate potential advantages of the low-bias high-plasma-density tool for further reducing process damage and increasing etch uniformity. Plasma diagnostics in this tool will provide additional validation of the electron-impact cross section set used in the plasma-chemistry models.

Empirical characterization of etching performance in SF_6 and CF_4 as well as literature survey of polymer-deposition and surface damage issues that arise in CF_4 -silicon etching systems led to the elimination of CF_4 as a candidate reagent in the etching process. We also studied Cl_2 -based RIE etching because literature accounts showed a beneficial etch-rate dependence which we attempted to exploit to obtain a self-limiting process with superior uniformity. However, we soon discovered an undesirable increased etch rate in the vicinity of the silver masks which led to unacceptable non-uniformity.

The self-aligned selective-emitter (SASE) plasma-etchback and passivation process for silicon solar cells was chosen as the experimental vehicle on which to demonstrate the plasma-processing concept. The key to the success of the SASE process lies in finding an etching technique that results in uniform emitter etchback while avoiding both silver gridline and silicon surface damage. We investigated Si etch rates and uniformity for a wide range of RIE parameters using combinations of SF_6 and Ar gases. Uniformity was monitored by measuring emitter sheet resistance over the full 130-cm^2 area of commercial silicon PV wafers after the etchback. Gridline damage was monitored

visually and by extracting the cell series resistance from dark I-V data. Surface damage was monitored by measuring the emitter saturation current density (J_{oe}) on high-resistivity float-zone wafers after passivation with a PECVD-nitride film. Wafers with similar emitter diffusion profiles that have lower values of J_{oe} have less surface recombination.

We succeeded in finding a set of parameters for rf-power, flow rate, pressure and gas composition, which resulted in negligible gridline damage, good uniformity, and minimal surface damage. The RIE etch resulted in a slight discoloration of the gridlines, but no noticeable effect on series resistance. Commercial wafers from Siemens and Solarex have a sheet resistance after diffusion of around $50 \Omega/\square$ with a standard deviation of 5%. After etchback, the commercial wafers were within 10% of the target value of $100 \Omega/\square$ over the full area of the wafers. While slightly higher than the starting non-uniformity, 10% represents an acceptable level of variation for this process. The results of J_{oe} measurements on bifacially diffused high-resistivity float-zone wafers are shown in Table 1.

Table 1. Average $J_{oe} \pm$ standard deviation in fA/cm^2 for 4 high-resistivity wafers that were phosphorus-diffused at Sandia. The wafers in the top row were diffused to a level of 100 ohms/square and were not etched back. The wafers in the bottom row were diffused to a sheet resistance of 44 ohms/square and RIE etched to 100 ohms/square.

Process	Thermal oxide	PECVD-nitride + FGA	Bare Si surface
Diffused to $100 \Omega/\square$	216 ± 9	205 ± 10	617 ± 62
Diffused to $44 \Omega/\square$ etched back to $100 \Omega/\square$	241 ± 5 ($40 \Omega/\square$)	221 ± 10 ($100 \Omega/\square$)	768 ± 143 ($100 \Omega/\square$)

Comparing the first two columns of J_{oe} values in the top row shows that the passivating quality of our PECVD-nitride is as good as that of our high-quality thermal oxide. In fact, the value of $205 fA/cm^2$ obtained with our direct plasma reactor compares favorably with the $110 fA/cm^2$ value obtained on $100 \Omega/\square$ emitters by other researchers who used a remote plasma reactor to obtain record-low values of surface recombination velocity. We expect to reduce the value of J_{oe} we obtain further by using the results of PECVD modeling predictions and a systematic parameter space investigation. The somewhat higher value of $221 fA/cm^2$ obtained on RIE etched-back wafers shows that any damage caused by the etchback has only a marginal effect on emitter passivation. While this small amount may be acceptable, aspects of our modeling work will be directed at reducing this damage further.

We have assembled gas-phase and surface-etch chemistry mechanisms for medium pressure (~ 1 torr) plasma etching of silicon in SF_6 plasmas and have used these mechanisms in a well-stirred plasma-reactor model to predict plasma composition and etch rates. These initial model results indicated that the plasma operating conditions chosen for the experimental study corresponded to a weakly dissociated, highly

electronegative plasma regime. This information has helped determine the appropriate diagnostics measurements that will be made to test and validate the chemistry model.

The plasma diagnostics group is continuing with the plasma and RF electrical characterization of the Vacutek RIE and CVD reactors. Probe measurements have confirmed the model predictions that the electron density is very low and highly electronegative. In addition to the stated goals for the first year, we also spent some time investigating the feasibility of an in-situ, real time, etch stop monitor after conversations indicated the need for a reliable method of determining when the etch had proceeded far enough. That investigation was suspended when it was determined that it was not feasible given our limited optical access to the wafer surface and project budget.

As a preliminary to the Langmuir probe measurements, we performed measurements of the spatially resolved ion saturation current (proportional to the electron density). Ion saturation current measurements of the spatial uniformity of plasma can be used to verify trends in the model predictions of electron density, improve the uniformity of the discharge and identify regions of plasma instability that can lead to non-uniform processing. An example of a probe measurement is shown in Figure 2 for a range of plasma powers near the empirically determined optimum.

Figure 2. Ion saturation current as a function of position in the plasma above the wafer in the Vacutek reactor. The location of the wafer holder is the long black line at the bottom of the figure while the wafer location is shown as the shorter black line on top of the holder.

These measurements were taken radially across the plasma approximately 2.5 cm above the wafer surface. In general, the plasma was highly nonuniform and asymmetric for these operating conditions. In addition, we observed some very erratic behavior in the saturation current in the vicinity of $r = 2$ cm for some plasma powers. This is the edge of the wafer and under some conditions, we have observed “plasma balls,” regions of the

enhanced optical emission, at the edge of the electrode. For most processes, operation in this parameter space should be avoided since reproducibility and / or uniformity can be difficult to maintain.

Because there is a theoretical basis for believing that reduced surface damage and increased uniformity should be expected using the high-density inductively coupled plasma (ICP) Plasmatherm reactor, we have begun measurements in this reactor which will be investigated in the second year. In preparation for these measurements, we have conducted a preliminary survey of the plasma characteristics in the ICP system. As shown in Figure 3, the electron density as a function of radial position is relatively constant for these plasma conditions (a prerequisite for uniform etching). However, under most other tool conditions the discharge was unstable and nonuniform. The Langmuir probe can be used to identify regions of plasma uniformity and stability within a large operational space.

Figure 3. In contrast to the Vacutek results, the plasma density in the ICP reactor was found to be more uniform.

In summary, all first-year technical milestones from the original proposal were met on schedule. Appropriate models for process and reactor modeling were developed. Because single-wafer reactors were selected, an investigation of batch size was precluded. In the second year, we propose additionally to make Langmuir probe measurements (electron density, electron temperature and plasma potential), and optical emission surveys in the ICP plasma system. Since plasma species are important in defining a starting point for an adequate computer model, we also have the capability to perform laboratory measurements of plasma species that are critical to improving our understanding of the important gas phase mechanisms in SF_6 etching and benchmarking the codes.

SECOND-YEAR ACCOMPLISHMENTS

Empirical Plasma-processing Development

We are using solar cell processing as an experimental vehicle to improve large-area plasma-processing capabilities and predictive models for use throughout the weapons complex. In order to zero-in on the regions of the parameter space which merit close study, we have empirically optimized the solar cell process by using statistical, multifactor experimentation. Figure 4 shows a response surface of a parameter inversely proportional to surface passivation quality. By use of statistical techniques, we were able to efficiently locate the plasma-processing parameter set which produces the best device performance, and could then apply our modeling and measurement efforts to the relevant parameter range.

Figure 4. Contour plot showing response of recombination current (J_{oe}) to the power (W) and pressure (mT) during NH_3 -treatment with a protective-nitride thickness of 10 nm. J_{oe} ranges from 216 in the lower left corner to a minimum of 161 fA/cm^2 near the upper right corner. The duration of the NH_3 hydrogenation was 20 minutes.

We were able to use these optimized deposition conditions on complete solar cells and obtained a 7% increase in power output compared to the standard industrial process. This is a significant improvement for commercial solar cell production, and is of considerable interest to the PV industry if it can be implemented cost-effectively. Sandia has applied for a patent on this process.

Plasma Characterization Experiments

Development of accurate models of the plasma etch process requires experimental information to validate the mechanisms in the code. During the past year, we have characterized the electron density, electron temperature and ion density using Langmuir probes and the plasma species using mass spectroscopy. Due to the challenges presented by the low plasma electron density in the parameter range of interest, we have spent some time developing double probe techniques that will work in the polymer depositing discharges and have applied those techniques to measurements in laboratory plasmas. In general, the technique is robust and provides reliable information on the spatially resolved electron density, temperature and positive ion density.

In addition to the plasma electrical characterization, we have had good success making ion and neutral measurements. These measurements were performed on the Plasma-Therm reactive ion etch (RIE) tool located in the CSRL in gas mixtures containing SF_6 and Ar. These measurements were performed over a large parameter space of power, pressure without a Si wafer (to provide a background reference) and with a Si wafer. As shown in Figure 5, the mass spectra are very rich. There are species from SF_x , S_xF_x , $\text{Si}_x\text{Si}_y\text{F}_z$ and a few $\text{C}_x\text{Si}_y\text{F}_z$. As expected, there are some very large differences in the plasma species as a function of discharge condition. We note that the dissociation of the SF_6 is fairly small for these plasma conditions which leads to a large number of radicals that can modify the surface etch process. In addition, for some of the larger molecules, the scaling with increased rf power indicates that they are stable in the plasma and must be included in the models. This in turn increases the complexity of the required models.

Figure 5. Mass spectrum of a 200 W SF_6 discharge during etching of silicon showing the large number of gas phase radical species.

Mechanism Development

Much progress was made in developing models for the plasma processes, which are being explored in this project. For the SF_6 etch of silicon, a chemical mechanism that includes 26 species and over 150 reactions has been produced. Calculations using this model compare favorably with probe measurements made on SF_6/Ar plasmas and are in modest agreement with mass spectrometry measurements of gas-phase species in pure SF_6 plasmas. Figure 6 shows the measured mole fractions of three species derived from the mass spectrometry measurements (solid lines) compared to model calculations (dashed lines) vs. rf power. The trends are correctly modeled, but more model refinement will be needed to improve the absolute agreement.

Figure 6. Measured and calculated plasma radical species for a nonetching SF_6 discharge. (For clarity, only a fraction of the plasma species are shown.)

A mechanism was also developed for the NH_3/N_2 plasma used for device passivation. By assuming that passivation efficiency is related to the hydrogen atomic concentration in the plasma, we were able to compare the results of the designed-experiment matrix of recombination current vs. plasma pressure and power. Some of the trends were reproduced, but the model still needed to be improved before it was considered predictive.

THIRD-YEAR ACCOMPLISHMENTS

SASE Cell Processing

We used the silicon-nitride deposition parameters that produced the minimum J_{oe} values obtained from Figure 1 in the processing of 130-cm^2 Solarex cells. The cells were processed up through gridline firing on the Solarex production line and sent to Sandia for

nitride deposition. We investigated whether shorter NH_3 -treatments would retain the benefits of surface passivation. Results of illuminated IV testing are shown in Table 2.

Table 2. Six SASE sequences were applied to 12 Solarex mc-Si cells using wafers from the same ingot as the controls. Illuminated cell IV data $\pm$ standard deviation are normalized to a constant transmittance to account for the additional 1.1% spectral-weighted absorbance in the nitride.

Eff. (%)	J_{sc} ..	V_{oc} (mV)	FF (%)
90 sec. RIE, 1-step SiN, FGA			
12.3 $\pm$ 0.4	30.5 $\pm$ 0.0	565 $\pm$ 4	71.6 $\pm$ 1.6
90 sec. RIE, 3-step SiN, 5 min NH_3, FGA			
12.9 $\pm$ 0.1	30.6 $\pm$ 0.1	573 $\pm$ 1	73.5 $\pm$ 0.4
90 sec RIE, 3-step SiN, 10 min NH_3, FGA			
12.4 $\pm$ 0.0	30.3 $\pm$ 0.0	570 $\pm$ 0	72.0 $\pm$ 0.0
150 sec RIE, 1-step SiN, FGA			
12.1 $\pm$ 0.5	30.1 $\pm$ 0.0	562 $\pm$ 7	71.3 $\pm$ 2.2
150 sec RIE, 3-step SiN, 5 min NH_3, FGA			
12.9 $\pm$ 0.2	30.4 $\pm$ 0.3	576 $\pm$ 4	73.5 $\pm$ 1.4
150 sec RIE, 3-step SiN, 10 min NH_3, FGA			
13.0 $\pm$ 0.2	30.4 $\pm$ 0.0	577 $\pm$ 2	74.0 $\pm$ 0.9
Control Cells: No emitter etchback, TiO_2 ARC			
12.6 $\pm$ 0.0	30.2 $\pm$ 0.1	569 $\pm$ 0	73.5 $\pm$ 0.0

The first three groups of cells were not etched back sufficiently, because the etch duration did not account for etching through a thermal oxide that grew on the cells during gridline firing. These cells do not show consistent improvement over the controls.

The second three groups used a longer 150-second RIE-etch that removed the thermal oxide and then etched the emitters from their starting sheet resistance of 50 Ω/sq to 100 Ω/sq . The 1-step cells show a drop in performance compared to the controls, in agreement with our J_{oc} results that showed poorer passivation by a 1-step nitride. Once the emitter is etched back to 100 Ω/square , it requires excellent surface passivation to avoid excess surface recombination.

Figure 7. IQE for cells described in Table 1.

The 3-step cells show significant improvements, especially in V_{OC} , suggesting longer diffusion lengths from bulk defect passivation. Internal quantum efficiency (IQE) of these cells, showing both improved red and blue response is shown in Figure 7.

All the nitride passivated cells show similar red and blue response, consistent with their similar J_{SC} values. The J_{SC} is no greater than that of the control cell because the increase in IQE is compensated by parasitic absorption in the nitride, which is due to the high refractive index of 2.2 used to minimize reflectance. Another series of SASE cells were processed using a lower refractive index of 2.12 to reduce the spectrally weighted absorbance to 0.5%. Normalized IV data for these cells are shown in Table 3.

Table 3. Three SASE sequences were applied to seven Solarex mc-Si cells using matched material from the same ingot as before. Illuminated IV data are shown below normalized to the transmittance of the control cells.

Eff. (%)	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)
140 sec RIE, 3-step SiN, 5 min NH₃, FGA			
12.9±0.2	31.1±0.1	572±3	72.7±0.3
140 sec RIE, 3-step SiN, 10 min NH₃, FGA			
13.1±0.0	31.4±0.1	574±0	73.0±0.1
140 sec RIE, 3-step SiN, 20 min NH₃, FGA			
12.2±0.4	31.2±0.1	563±5	69.5±1.5
Control Cells: No emitter etchback, TiO₂ ARC			
12.3±0.1	30.8±0.0	558±2	71.4±0.4

The SASE cells have consistently higher J_{SC} than the controls, because now the increased IQE due to passivation is not lost due to excessive parasitic absorption. The cells that

received 10 minutes of NH_3 -hydrogenation performed the best, exceeding the controls by almost a full percentage point due to the large improvement in V_{OC} . However, improvement in V_{OC} is reduced for the cells that received a 20-minute NH_3 -exposure. These cells also suffered a loss in fill factor due to an increase in diode ideality factor.

The use of an optimum-duration, NH_3 -plasma hydrogenation treatment was found to be crucial to the increased performance. As the data in Figure 8 show, the fill factor and open-circuit voltage increase for durations up to 10 minutes, and then decrease due to higher non-ideal diode recombination, probably due to accumulated plasma-induced surface and gridline damage. This is consistent with the results of the emitter passivation studies because even though they predicted lower J_{0e} values for longer durations, they were performed on bare Si wafers and did not incorporate the effect of the plasma on the gridlines.

Figure 8. V_{OC} and FF peak at NH_3 -plasma hydrogenation durations of 10 minutes.

Silicon-Nitride Refractive Index Model

The PECVD deposited silicon nitride film has been demonstrated to be an effective ARC material. In addition, some experimental results indicate that the PECVD deposited nitride layer also provides good surface and bulk passivation for silicon solar cells. As it will be presented later, the refractive index of silicon nitride deposited by PECVD method can be varied for a wide range from 1.9 to 2.4, depending on the silicon to nitrogen ratio in the processing gases. This feature provides a unique opportunity for depositing multiple-layer ARC with the same material. In this section, we will report a systematic approach in development of different refractive index silicon nitride materials.

It is well known that the refractive index of a material can be correlated to the electronic polarizability through the Clausius-Mossotti equation

$$\frac{N\alpha}{3\epsilon_0} = \frac{n^2 - 1}{n^2 + 2}$$

where N is the electron density in the solid (number of electrons per unit volume), α is the electronic polarizability ($\alpha = 4\pi\epsilon_0 r^3$), n is the refractive index of the material, and ϵ_0 is the permittivity of free space. According to the above equation, the refractive index depends upon composition of an optical material; the larger the atomic/ionic radius, the greater is the electronic polarizability, and the higher is the refractive index. There has been a good linear correlation between refractive index and electron density in various glasses reported in the literature. Based on this concept, the refractive index of silicon nitride ($\text{Si}_{3+x}\text{N}_{4-x}$) can be varied with the silicon to nitrogen ratio in the material.

From a processing perspective, we can achieve this goal by varying the composition of reaction gases in the thin film deposition process. The reaction gases used for the nitride deposition are a 5% mixture of silane in helium, nitrogen, and anhydrous ammonia. Plasma deposition was performed in the Plasma Therm 790 reaction chamber at 350 °C, with total pressure of 1500 mTorr and a power of 20 watts. Since nitrogen can not be effectively dissociated under our operation conditions, the changes in the nitrogen content in the silicon nitride film will primarily rely on nitrogen atoms dissociated from the ammonia source. To keep the deposition in a reasonable rate, the ammonia flow rate is fixed at maximum (i.e. 14.5 sccm). By varying the flow rate of the silane mixture, with a total flow rate of nitrogen and silane up to 1200 sccm, the silicon to nitrogen ratio in the reaction gases can be changed. We expect the refractive index of PECVD deposited silicon nitride to increase as the silane to ammonia ratio in the reactor chamber increases.

Figure 9. The change of refractive index of PECVD-nitride as a function of the silicon to nitrogen ratio (or SiH_4/NH_3).

A linear relationship between the refractive index of plasma deposited silicon nitride film and the silicon to nitrogen ratio was observed. Results indicate that the refractive index

of the nitride film can be varied from 1.95 to 2.45 within this processing space. Since bonding between silicon and nitrogen is also more covalent in nature (less than 22% ionic character), the difference in electronic polarizability between S-Si and Si-N will be negligible relative to the great changes in electron density as the composition of the film varies. Therefore, the observed linear relationship can be attributed to the increase in electron density in the nitride film as the composition in the film gets more silicon rich. By extrapolation or interpolation technique, different refractive index layers of PECVD-nitride films can be sequentially deposited to form a multi-layer ARC.

Modeling a Dry Etch Process

We have been developing plasma models to simulate each of these processes in sufficient detail that they can be used for process development and control. Reported here is the modeling of the SF₆ RIE plasma. In order to refine the chemical mechanism, a variety of diagnostic measurements were performed on the SF₆ plasma, including determination of silicon etch rates, mass spectrometry probes, Langmuir probe measurements of ion saturation currents, and gas temperature with a fluoroptic probe.

The plasma simulations were done using the computer code AURORA [2], which employs CHEMKIN [3] and predicts the steady-state properties of a reactor for plasma-chemistry systems. Our approach to plasma modeling is to incorporate all the known chemistry and physics, and make best estimates of the unmeasured, but expected, chemistry. For example, much of the plasma behavior is governed by electron collisions with SF₆. We rely heavily on cross section measurements [4,5,6] for the many channels such as ionization to give SF₅⁺, SF₄⁺ etc., fragmentation to give SF₅, SF₄, etc., attachment to give SF₆⁻, and vibrational and electronic excitation of the SF₆. The cross sections (σ) are measured vs. electron energy, and the predicted rate of a given reaction is calculated as the overlap of the electron energy distribution and the σ vs E curve. We convert the reported σ data into Arrhenius form for computational ease. This introduces a small error, which is deemed negligible relative to uncertainty in the actual electron energy distribution in the plasma.

Reaction rates for the neutral reactions are very poorly known. Fortunately, the low densities of radicals in the plasma, and low total pressure result in relatively minor contribution from many of the expected radical-radical reactions. Three-body recombination reactions such as F + F + M = F₂ + M are expected to play a role even at these reduced pressures. The 3-body rates that have been reported are typically not obtained using SF₆ as M. Therefore, it is necessary to estimate the 3-body rates for the many potential 3-body reactions and these rates are adjusted for best fit.

The importance of fluorine-based plasmas for etching silicon has led to some good fundamental work on the surface reactions of F atom on silicon. Our surface mechanism proposes a predominant reaction of F atoms with surface silicon to give SiF₂ groups and then further reaction to eliminate SiF₄ gas similar to the treatment of Flamm [7]. Ion assisted etch is included explicitly by allowing each positive ion to remove SiF₄. The calculation distinguishes reaction at the chamber walls from silicon and uses a F atom

wall recombination rate based on that estimated by Ganguli, et al., [8] but adjusted for best fit. Our model incorporates 27 gas phase species including neutrals, electrons, positive and negative ions and a reaction mechanism with 138 gas-phase and 26 surface reactions.

Etching of photovoltaic cells and most diagnostics are done on a PlasmaTherm 790 reactor, which is a parallel-plate system operating at 13.56 MHz. The reactor was instrumented with a differentially pumped mass spectrometer which probes the plasma gas directly with minimum wall recombination. Mass spectra are obtained for a range of power and pressure conditions with and without a silicon wafer in place. A Langmuir probe is used to obtain ion saturation current for a range of plasma conditions. In order to determine the silicon etch rate, 100 mm patterned wafers are etched and measured with profilometry at five locations. No significant radial non-uniformity of etch rate is observed.

On a separate research reactor, also capacitively-coupled, parallel plate and 13.56 MHz, the gas temperature of the SF_6 plasma was measured by fluoroptic probe. The reactor geometry is adjusted in the model calculations to allow comparison with this data.

We have developed a plasma chemistry model that gives a reasonably good fit to the data sets. Figure 10 shows a comparison of the etch rate data measured to the calculated rates graphed vs. pressure for five plasma powers. The overall trends are reproduced quite well, with a peak in etch rate observed at high power and intermediate pressure. At low power, the etch rate falls rapidly with increasing pressure. The model explains this falloff as due to electron capture by SF_6 depleting electrons so strongly, that the plasma is almost extinguished. In fact, at the highest pressures and low power, the calculation fails to converge because all electrons in the plasma are captured by SF_6 and no plasma solution can be found.

Figure 10. Etch rate of silicon in SF_6 plasma. Experiment (solid lines) compared to model calculation (dashed lines). Curves are shown for powers (top to bottom) 100, 75, 50, 25, and 15 Watts.

The overall shape of the etch curves is predominantly the result of changes in the electron density, N_e , and temperature T_e . At high power and low pressure, N_e is highest but T_e is low. As pressure increases, N_e falls due to capture, and T_e increases as the rf power is coupled to fewer electrons. The increase in T_e leads to an increased production of F atoms from the reaction $e^- + \text{SF}_6$ which has a significant activation barrier. Eventually at high pressure, the loss of electrons to form negative ions dominates and F concentration falls. At low power, electron capture and negative ion formation tend to extinguish the plasma, with this phenomenon starting even at low pressure.

While overall trends in the etch data are determined by electron- SF_6 collisional phenomena, at high pressure and low power the calculation becomes sensitive to almost every reaction in the model. As N_e falls, small changes in any rate constant lead to major changes in N_e and T_e and hence the F atom density and etch rate. This effect probably will correspond to instability and difficulty in achieving reproducible etch rates. Small changes in wall cleanliness or temperature, for example, would be expected to influence etch rate. The model suggests that for manufacturing robustness, the plasma etch process should be operated in a parameter regime away from this metastable condition.

Figure 11 shows three graphs comparing plasma diagnostic measurements to the calculation. The agreement is not perfect, but the trends and magnitudes are reproduced quite well. Although the gas temperature measurements were obtained on a different reactor with much smaller plasma volume, and hence higher power volume-density, the agreement is quite good. The break in the measured temperature above 40 watts is accompanied by a visual change in the plasma emission, and probably represents a reduced power density as the plasma volume increases.

Figure 11. Comparison of calculation (dashed line) with experiment. Top: Fluoroptic probe measurement of gas temperature. Middle: Mass spectrometry measurement of SF₆. Lower: Langmuir probe measurement of ion saturation current.

The comparison with mass spectrometer measurements of SF₆ mole fraction is the most direct, because fragmentation patterns in the ionizer can be calibrated directly. Trends in other mass signals corresponding to the radicals SF₄ and SF₂ are used for fitting, but absolute densities of these species are less certain.

In order to compare the ion saturation current measurements, the calculated density of all 8 positive ions is used with the calculated T_e , and the Bohm velocities, v , for each ion, and the formula $I_{sat} = N_i * e * v$. Agreement with the measurements is quite good.

SUMMARY

We have studied a dry process for plasma-etchback of the emitter in full-size multicrystalline silicon cells. The plasma is pure SF_6 in a capacitively-coupled parallel plate commercial reactor. Plasma diagnostic measurements include etch rates, Langmuir probe measurements of ion saturation currents, mass spectrometric probes of the plasma gas and gas temperatures. A plasma model is developed and tested against these data. We obtained reasonable agreement with the measurements. From an analysis of the model results for the fall-off in etch rate at high pressure, we conclude that the plasma is likely to become very sensitive to minor system perturbations at high pressure and low power. Operation in this regime is liable to result in reduced process stability and reproducibility. Further refinement of the model will be possible as more kinetic data and diagnostic measurements become available; however, the current model should be reliable enough to guide process scale-up and optimization.

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APPENDIX A

Publications, Patents, and Technical Advance Disclosures for LDRD Report

Publications

Ruby, D. S., C. B. Fleddermann, M. Roy and S. Narayanan, "Self-Aligned Selective-Emitter Plasma-Etchback and Passivation Process for Screen-Printed Silicon Solar Cells", **Technical Digest of the 9th International Photovoltaic Science and Engineering Conference**, Miyazaki, Japan, November 1996, pp. 111-112.

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Ruby, D. S., P. Yang, S. Zaidi, S. Brueck, M. Roy and S. Narayanan, "Plasma Etching, Texturing, and Passivation of Silicon Solar Cells", **Proc. of NCPV Project Review Meeting**, Denver, CO., September 1998.

Ruby, Douglas S., Pin Yang, Saleem Zaidi, Madhu Roy, S. Narayanan, "Plasma Texturing, Etching and Passivation of Multicrystalline Silicon Solar Cells", **Renewable and Advanced Energy Systems for the 21st Century**, Maui, HI, April 1999. Winner of 1999 Best Paper Award.

R. J. Buss, D. S. Ruby, G. A. Hebner and P. Yang, "Modeling a Dry Etch Process for Large-Area Devices", **9th Workshop on Crystalline-Silicon Solar Cell Materials and Processes**, Breckenridge, August 1999

Patents

A United States Patent entitled "SILICON SOLAR CELLS MADE BY A SELF-ALIGNED, SELECTIVE-EMITTER, PLASMA-ETCHBACK PROCESS" was issued on February 16, 1999 as patent number 5,871,591. The inventors are D.S. Ruby, J.M. Gee, and W.K. Schubert.

Technical Advance Disclosure

Technical Advance Disclosure: Improved Silicon Solar Cells made by Self-Aligned, Selective-Emitter Plasma Etchback Process, SD-5829.1, S-89,721. The inventors are Douglas S. Ruby and Saleem H. Zaidi.

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